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INVESTIGATION OF AMPHIPATHIC WATER-SOLUBLE POLYMERS AS FLOCCULANTS AND FLOTATION AIDS IN DOMESTIC WASTEWATER TREATMENT

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Standard Brands Chemical Industries, Incorporated
Dover, Delaware

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INVESTIGATION OF AMPHIPATHIC WATER-SOLUBLE POLYMERS AS FLOCCULANTS AND FLOTATION AIDS IN DOMESTIC WASTEWATER TREATMENT

by

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for

The Advanced Waste Treatment Research Laboratory

Robert A. Taft Water Research Center

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FOREWORD

In its assigned function as the Nation's principal natural resource agency, the United States Department of the Interior bears a special obligation to ensure that our expendable resources are conserved, that renewable resources are managed to produce optimum yields, and that all resources contribute their full measure to the progress, prosperity, and security of America -- now and in the future.

This series of reports has been established to present the results of intramural and contract research studies carried out under the guidance of the technical staff of the FWPCA Robert A. Taft Water Research Center for the purpose of developing new or improved wastewater treatment methods. Included is work conducted under cooperative and contractual agreements with Federal, state, and local agencies, research institutions, and industrial organizations. The reports are published essentially as submitted by the investigators. The ideas and conclusions presented are, therefore, those of the investigators and not necessarily those of the FWPCA.

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ABSTRACT

Five amphipathic polymer systems (strong and weak anionic, strong and weak cationic, and nonionic) were prepared by two techniques giving lower and higher molecular weights. The various polymer systems were characterized by Brookfield viscosity and foaming tendency in aqueous solution.

These polymers were evaluated for efficiency in removing solids from unsettled raw sewage using three methods: a simple continuous flotation cell, a static pressurized water flotation unit, and a conventional jar test.

The nonionic and anionic amphipathic polymers showed little or no flocculating ability; only the cationic types were effective. Qualitatively the strong cationic polymers (dimethylaminoethyl methacrylate/ethyl bromide quaternary salt as comonomer) were more effective than the weak cationic polymers (dimethylaminoethyl methacrylate/HCl salt as comonomer). Effectiveness increased with increasing % quaternary comonomer. There is slight evidence that the presence of an oleophilic comonomer (N-n-octadecyl acrylamide) improved the efficiency of the strong cationic polymer system.

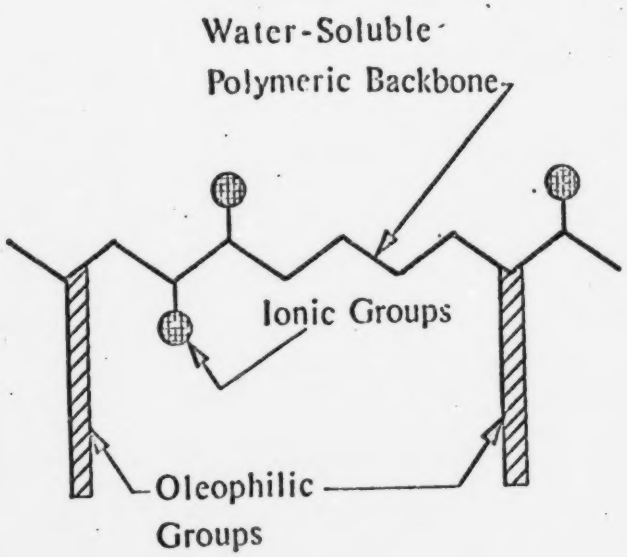
A commercially available cationic flocculant was used as a reference polymer for comparison purposes. In most cases this reference polymer was superior to the amphipathic polymers at a given dosage.

INTRODUCTION

The broad objective of this investigation was to find new, commercially feasible, synthetic water soluble polymers which would show improved flocculating ability for suspended matter in sewage.

The effectiveness of many high molecular weight water soluble polymers in flocculating suspended particles is well known. The bridging mechanism proposed by La Mer and coworkers accounts for the increasing flocculating efficiency with increasing molecular weight.

In view of the variety of colloidal surfaces encountered in sewage, the investigation of amphipathic polymeric flocculants could not be overlooked. The type of macromolecule proposed for study as a flocculant was a water soluble, surface active polymer with a high hydrophilic to hydrophobic ratio, in effect, a type of polymeric surfactant. A schematic prototype of an ionic amphipathic polymer is shown below.



It has been observed that "monomeric" surfactants at low concentrations can act as flocculants for suspended solids in water. By rendering the particle surface more hydrophobic, interparticle adhesion is achieved by Van der Waal (micellar) forces. This would indicate that an oleophilic group capable of micelle formation could function as another potential "hook" for flocculation.

The types of amphipathic polymers which were synthesized and tested are shown in Table I.

Table I Amphipathic Polymers

Charge Type	Copolymer Type
Nonionic	AMD/AMD-N-C_{18}
Strong Cationic	AMD/AMD-N-C_{18}/DMAEMA-EtBr
Weak Cationic	AMD/AMD-N-C_{18}/DMAEMA·HCl AMD/AMD-N-C_{18}/AMD-N-CH_2-NEt_2
Strong Anionic	AMD/AMD-N-C_{18}/SEMA
Weak Anionic	AMD/AMD-N-C_{18}/AA

AMD - Acrylamide

DMAEMA - Dimethylaminoethyl Methacrylate

SEMA - 2-Sulfoethyl Methacrylate

AA - Acrylic Acid

AMD-N-C_{18} - N-n -Octadecyl Acrylamide

EXPERIMENTAL - SYNTHESIS

MONOMER SYNTHESIS

Monomers were synthesized only when they were found to be commercially unavailable. Thus, it was necessary to prepare the following: N-n-octadecyl acrylamide (AMD-N-C_{18}), the ethyl bromide quaternary salt of dimethylaminoethyl methacrylate (DMAEMA·EtBr) and the hydrochloride salt of dimethylaminoethyl methacrylate (DMAEMA·HCl).

N-n-Octadecyl Acrylamide

N-n-octadecyl acrylamide was readily prepared by the reaction of n-octadecyl amine (Armeen 18D from Armour Chemicals) with acrylyl chloride (Borden Chemical) in toluene, using triethyl amine (Union Carbide) as HCl acceptor, according to the following reaction:

$$C_{18}H_{37}NH_2 + CH_2{=}CHC(=O)Cl \xrightarrow{Et_3N} CH_2{=}CHC(=O)NHC_{18}H_{37} + Et_3N{\cdot}HCl$$

Thus, 53.2 grams (0.2 moles) of n-octadecylamine (containing approximately 10% n-hexadecylamine), 24.2 grams (0.24 moles) of triethyl amine (dried over KOH), and 500 mls of toluene were placed in a liter reaction flask fitted with a stirrer, thermometer, condenser, and a dropping funnel. The temperature was elevated to 30°C in order to insure complete solution of the reactants. The resulting clear solution was subsequently cooled to 25°C and 20.8 grams (0.23 moles) of acrylyl chloride in 80 mls of toluene was added with vigorous agitation dropwise over an hour's duration. The triethylamine sale ($Et_3N{\cdot}HCl$) formed immediately as a fine white precipitate. The internal temperature was maintained at 25-30°C

during this period. At the end of the addition, the temperature was raised to 35°C for an additional 1 1/2 hours. Then 2.0 grams (0.05 moles) of sodium hydroxide dissolved in 5 mls of water was added in order to destroy any residual acrylyl chloride. Agitation was maintained for an additional forty-five minutes.

The reaction mixture was subsequently filtered through a Buechner funnel to remove the $Et_3N \cdot HCl$ ppt. The filter cake was found, however, to contain a considerable quantity of occluded product (N-n-octadecyl acrylamide). The product was recovered by extraction with toluene. Thus, the filter cake was slurried in 87 mls of toluene at 65°C containing 0.05 grams of MEHQ (monomethyl ether of hydroquinone) in order to inhibit polymerization, and filtered hot. The extraction was repeated with 25 mls of toluene containing 0.0125 grams of MEHQ. The combined extracts were cooled in an ice bath. The product crystallized as white waxy platelets, 30.8 grams vacuum dried at 50°C.

The filtrate from the original reaction mixture was concentrated in a rotary vacuum evaporator at 5 mm Hg. After cooling the resulting concentrated solution in an ice bath, an additional 20 grams of product was obtained for a total crude yield of 50.8 grams (79% yield). The crude products were combined and recrystallized from toluene. After vacuum drying the product had a mp of 71°C versus a literature value (1) of 69°C. Analyses showed:

	Theory	Experimental
% N	4.33	4.31
Mol. Wt. via Vapor Phase Osmometer	323	315
% C = C	7.4	8.3

Dimethylaminoethyl Methacrylate·Ethyl Bromide Quaternary Salt

Dimethylaminoethyl methacrylate (157.0 gms, 1.0 moles) (Alcolac Chemical), ethyl bromide (120.0 gms, 1.1 moles) (Matheson, Coleman, and Bell), and 100 gms of methanol, containing 0.05 gms of MEHQ to inhibit polymerization, were placed in a liter reaction flask. The temperature was maintained at 30°C under agitation for three hours. The methanol was removed under vacuum (5 mm Hg). The white solid product was washed with 150 mls of hexane and vacuum dried at 50°C. A yield of 263 gms (99% yield) was obtained. Analysis showed:

	Theory	Experimental
% N	5.32	5.34
% Br	30.4	28.6
% C = C	9.1	8.5

Dimethylaminoethyl Methacrylate - HCl Salt

One mole, 157.0 gms, of dimethylaminoethyl methacrylate and 108 gms of benzene were placed in a 500 ml reaction flask equipped with an internal thermometer, an above the surface inlet tube, reflux condenser, and magnetic stirrer. The inlet tube was connected to an HCl generator consisting of a 500 ml flask containing 117 gms (2 moles) NaCl and fitted with a dropping funnel containing 98 gms (1 mole) H_2SO_4. The HCl, generated by adding the H_2SO_4 dropwise to the NaCl, was introduced above the liquid surface of the stirred DMAEMA solution which was held at 15°C with an ice bath. Due to mechanical difficulties, it was necessary to filter off the white crystalline precipitate which formed and reexpose the filtrate to an additional

quantity of HCl. After three exposures a yield of 127 gms (66%) of hexane-washed, vacuum-dried white powder was obtained.

	Theory	Experimental
% Cl	18.1	18.6
% C = C	13.5	17.2

POLYMER SYNTHESIS

The technique of copolymerizing in a mutual solvent for the monomers and obtaining the polymer as a particulated precipitate is desirable since the product can be readily isolated by filtration and can be washed free of any unreacted monomers. Since reasonably high molecular weights are desirable from the standpoint of flocculating ability, it is important to use a solvent with a low chain transfer coefficient. For this reason tertiary butanol was selected. The catalyst used was azo-bisisobutyronitrile (AIBN) which is known to be a very efficient free radical catalyst as well as to produce linear type polymers. A typical polymerization recipe is shown below.

Table II Polymerization Recipe

Monomers	100 gms
t-butanol	900 mls
AIBN	0.05 gms
Temperature	80°C

The apparatus employed consisted of a reaction flask equipped with a reflux condenser, stirrer, internal thermometer, and an external hot water bath. The monomers and t-butanol (Shell Chemical) were charged into the reactor and heat was applied externally to bring the internal temperature to reflux (80°C). A nitrogen blanket

was maintained both during the heat-up as well as during the course of the polymerization reaction. The catalyst was injected into the reactor at the desired temperature as a 0.5% solution in t-butanol. Polymer was found to precipitate within 2 minutes of initiation. Reflux and stirring was maintained for three hours after initiation. The white polymer dispersion was filtered hot and washed with additional quantities of t-butanol. All polymers were subsequently dried in a 50°C vacuum oven. Polymer yields were generally found to be above 97%.

In general, relatively low molecular weight polymers were obtained with the above recipe. The effect of catalyst concentration was examined in the polymerization of acrylamide, Table III.

Table III Effect of Catalyst Concentration

Parts AIBN, phm*	(η)	Brookfield Viscosity (2% Aqueous Solution)
0.25	0.94	-----
0.20	1.08	-----
0.10	1.14	-----
0.05	1.30	7.5 cps

*phm = per 100 parts of monomer

Intrinsic viscosities, (η), were determined in 1N NaCl. Uncertainties in extrapolation make the absolute (η) values questionable. However, the expected trend to higher values with lower catalyst levels was exhibited. Catalyst concentrations below 0.05 phm were found to give low yields of polymer. At 0.05 phm AIBN, the Brookfield Viscosity of a 2% aqueous solution was found to be only 7.5 cps which is evidence of the polymers relatively low molecular weight when

compared to commercially available polyacrylamides.

Efforts were made to increase the polymer molecular weight by the use of a mixed solvent system. This is based on the assumption that the radical transfer constant with t-butanol solvent is too great to obtain high molecular weights.

Thus, the polymerization of acrylamide was investigated using t-butanol with benzene, toluene, or hexane as the polymerization media. It was found that only 5.5 volume per cent of t-butanol was required with either benzene or toluene in order to obtain monomer solubility in the polymerization recipe as shown in Table II. In the case of hexane 39 volume per cent of t-butanol was required.

Only a slight increase in molecular weight was observed from these mixed solvent systems, Table IV.

Table IV Effect of Mixed Solvent on Molecular Weight

Solvent	Brookfield Visc (2% Polymer Soln)
t-butanol	7.5 cps
t-butanol/hexane (89/11)	8
t-butanol/toluene (83.5/16.5)	8
t-butanol/benzene (39/61)	9

As seen in Table IV, the molecular weight increases slightly as the concentration of t-butanol decreases. However, at the polymerization temperature of 80°C, the chain transfer constant with solvent is of sufficient magnitude to result in a low molecular weight polymer. Although the monomer was found to be soluble in the benzene/t-butanol solvent at benzene concentrations above 61 volume per cent, the resulting polymers were found to be partially insoluble.

A series of non-ionic amphipathic copolymers, AMD/AMD-N-C_{18} (0.5 to 3.0% AMD-N-C_{18}), were also prepared using benzene/t-butanol (28, 50, and 61 volume per cent benzene) as the polymerization media. The polymers thus obtained were all found to be insoluble in water. The solubility was found to decrease with increasing benzene concentration in the reaction media as well as with the AMD-N-C_{18} monomer concentration. Thus, an AMD/AMD-N-C_{18} (97/3) copolymer prepared in benzene/t-butanol (28/72) solvent media would not even wet. This is clearly indicative that there is in the mixed solvent system, especially one containing benzene, a polymerization mechanisim which results in a highly crosslinked product. No further effort along this line was made.

One other approach was employed in order to obtain polymers of increased molecular weight. It is known that the catalyst, AIBN, when exposed to 3660A° UV radiation, readily decomposes at 23°C thereby initiating polymerizations. It is also known that the rate of chain transfer with the solvent is temperature dependent, decreasing with decreasing temperature.

The polymerization of acrylamide was thus investigated as a model using the recipe of Table II except that the reaction temperature was 35°C and the catalyst was decomposed by UV radiation. The polymerization reactions were carried out in Pyrex reaction flasks under a N_2 atmosphere. Exposure to the UV source was maintained for five hours. Although the reaction mixture was initially 23°C, the internal temperature quickly rose to 35°C under the influence of

the UV irradiation. No external cooling was applied during the course of the reaction. Unlike the thermal polymerization, it was found that 400 mls phm of additional solvent, t-butanol, was required during the course of the polymerization reaction in order to maintain a stirrable suspension. This is probably indicative of a smaller particle size suspension.

As shown in Table V, the UV polymerization of acrylamide is affected by both the intensity of the UV source as well as the catalyst concentration.

Table V UV Catalyzed Polymerization of Acrylamide

UV Intensity	AIBN Conc, phm	% Conversion	2% Brookfield Visc, cps
Low Medium*	.05	35	22
" "	.10	52	22
" "	.20	66	25
High Medium**	.05	77	14.5
" "	.20	100	17.5

*No rating available
**Blak-Ray Model B-100A, Ultra-Violet Products, Inc., rated at 8400 microwatts per cm^2 of 3660A^{o} radiation at 18 in.

The conversion of monomer to polymer was found to increase with increasing AIBN concentration, as well as the UV source intensity. The Brookfield viscosity (and thus the molecular weight, assuming a direct relationship) was found to be dependent upon the UV intensity, decreasing with increasing UV intensity. The Brookfield viscosity appears not to be appreciably affected by the AIBN concentration. In comparison with the thermal polymerization of acrylamide the viscosity (2% aqueous) increased 2 to 3 fold. Thus,

both the thermal recipe as shown in TableII and the UV modification were used to prepare the polymers used in this study. The concentration of AIBN used in the UV recipe was generally 0.1 parts phm.

EXPERIMENTAL - POLYMER CHARACTERIZATION

The various polymers in this study were characterized by measuring the foaming characteristics as well as the Brookfield Viscosities of their respective 2% aqueous solutions. The foaming characteristics of the polymer systems were measured by bubbling air, by means of an aquarium diffuser at a constant flow rate, through 100 mls of a 0.05% polymer solution in a 500 ml graduate cylinder for 3.5 minutes, at which time the foam height was measured.

Using both the thermal and UV recipes stated earlier, the following amphipathic polymer types were prepared: nonionic, cationic (strong), cationic (weak), anionic (strong), and anionic (weak).

NONIONIC POLYMERS

It was determined in the thermal recipe, that the maximum oleophile (AMD-N-C_{18}) concentration for the nonionic polymer system (AMD/AMD-N-C_{18}) with which water solubility could be obtained was 3%. The identical composition prepared with UV catalysis was found to be insoluble in water, thus indicating that a balance between oleophile concentration and polymer molecular weight is required. At an oleophile concentration of 2% or less, water solubility was obtained with the UV system.

Table VI Nonionic Amphipathic Polymers

Sample	AMD/AMD-N-C_{18}	Pzn. Type	2% Brookfield Visc, cps	Foam Height,* mls
003-18A	97/3	Thermal	210	225
B	98/2	"	138	150
C	99/1	"	10	100
D	99.5/0.5	"	9	70
003-34A	99/1	UV	596	270
B	98/2	"	18,700	365

*003-18 series used 0.025% polymer solution
003-34 series used 0.05% polymer solution

As shown in Table VI, the Brookfield Viscosity of the 2% aqueous solutions increased as the AMD-N-C_{18} content of the polymer increased. This increase in viscosity should not be interpreted as meaning that the polymer molecular weight increases with the oleophile content. This effect is primarily due to the intramolecular association of the n-octadecyl groups. An approximate 100 fold increase in 2% viscosity was observed with UV polymerization as compared to thermal polymerization. This is significantly greater than the corresponding 2 to 3 fold increase observed in the homopolymerization of acrylamide (Tables IV and V). Once again it cannot be construed that a larger increase in molecular weight is obtained with increasing oleophile content. The extent of the increase in molecular weight using the UV system is probably relatively constant with the great increase in viscosity due primarily to the association of the oleophile moiety.

CATIONIC POLYMERS

Surface tension (water-air interface) measurements were conducted on both the thermal initiated nonionic and the cationic polymer systems using a du Nouy Tensiometer. Plotting surface tension versus polymer concentration, all systems exhibited a discontinuity, typical of a critical micelle concentration (CMC). Unlike monomeric emulsifiers, the surface tension was found to increase at concentrations beyond the CMC. This phenomenon is perhaps due to hydrogen bonding between the polymeric micelles and/or to the increasing viscosity of the polymer solution with increasing total solids.

Table VII Surface Tension of Aqueous Polymer Solutions

AMD/AMD-N-C_{18}/DMAEMA·EtBr	CMC (Wt %)	γ @ CMC (Dynes/cm)
99/3/0	0.76	70.3
98/2/0	0.76	70.2
99/1/0	1.02	71.0
99.5/0.5/0	1.20	69.6
45/5/50	4.0	68.3
35/5/60	2.6	69.8
67/3/30	0.78	69.3
68/2/30	0.71	68.6

($\gamma_{distilled\ H_2O}$ @ 23.5°C = 72.2 dynes/cm)

As seen in Table VII, the CMC of the nonionic polymers system decreases with increasing oleophile content in agreement with the aforementioned postulate regarding the association of the N-n-octadecylacrylamide moiety. The incorporation of the cationic quaternary monomer (DMAEMA·EtBr) was found to raise the CMC as compared to the nonionic (AMD/AMD-N-C_{18}) copolymer system. The surface tension depression at the CMC was only 2 to 3 dynes/cm and 3 to 4 dynes/cm for the nonionic and cationic systems respectively.

Table VIII Strong Cationic Amphipathic Polymers

Sample	AMD/AMD-N-C_{18}/ DMAEMA·EtBr	Pzn Type	2% Brookfield Visc, cps	Foam Height, mls*
003-20A	55/5/40	Thermal	56**	100
B	45/5/50	"	38**	50
C	35/5/60	"	31**	60
D	66/4/30	"	58	185
E	67/3/30	"	56	300
F	68/2/30	"	73	500 plus
003-45A	55/5/40	UV	360**	0
B	45/5/50	"	320**	0
C	35/5/60	"	132**	0
D	66/4/30	"	175**	85
E	67/3/30	"	120**	180
003-52A	95/0/5	Thermal	9	0
B	75/0/25	"	10	0
D	70/0/30	"	18	0
E	60/0/40	"	15	0

* 0.05% polymer solution
** Some insolubles @ 2% concentration, completely soluble at high dilution.

The foaming tendency was not found to be related to the surface tension depression, but related to the polymer composition and polymer molecular weight (Tables VI and VIII). In the nonionic system the frothiness of the polymer solution was found to increase with increasing oleophile content. In the cationic system the foam height was found, at a constant oleophile content, to increase as the cationic content decreased. In contrast with the nonionic polymers, the strongly cationic polymers (at constant cationic content) showed decreasing foam height with increasing oleophile content. It was also observed that the foaming tendency for a given polymer composition decreased with increasing polymer molecular weight in the cationic system. In the nonionic system the reverse was observed.

For comparative evaluation a series of cationic copolymers

(AMD/DMAEMA·EtBr) without the oleophilic moiety were prepared. As expected these polymers showed no tendency to foam and were much lower in viscosity than the corresponding polymers containing the oleophilic moiety (Table VIII).

The cationic terpolymers both strong and weak (Table VIII and IX) exhibited similar viscosity and foaming behavior. A similar decrease of foam height with increasing cationic content was observed. Also, at constant cationic content an increase in foaming efficiency with decreasing oleophile content was generally observed.

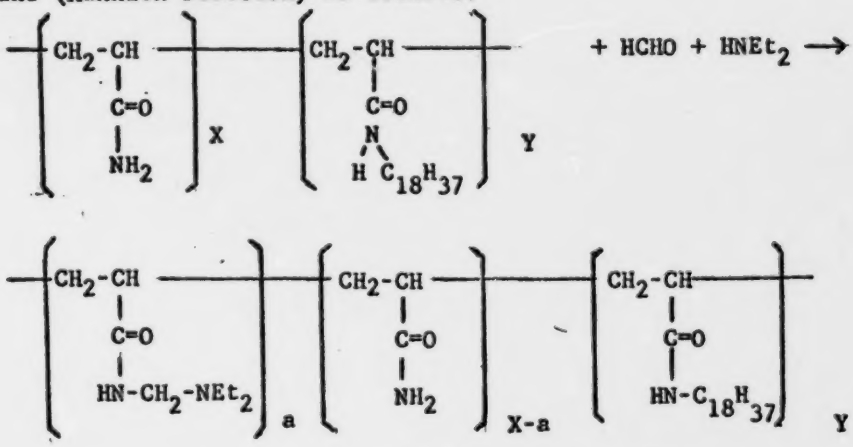
Table IX Weak Cationic Amphipathic Polymers

Sample	AMD/AMD-N-C_{18}/ DMAEMA·HCl	Pzn Type	2% Brookfield Visc, cps	Foam Height, mls*
003-41A	77/3/20	Thermal	67	305
B	67/3/30	"	94	236
C	57/3/40	"	43	425**
D	76/4/20	"	300	425**
E	66/4/30	"	94	475**
F	56/4/40	"	84	425**
003-51A	77/3/20	UV	90***	225
B	67/3/30	"	160***	260
C	57/3/40	"	93***	230
D	76/4/20	"	310***	200
E	66/4/30	"	360***	75
F	56/4/40	"	340***	70

* 0.05% polymer solution
** Foam showed no sign of breaking at end of 3.5 minutes
*** Slightly insoluble @ 2% polymer solution

The weak cationic moiety (DMAEMA·HCl) was found to possess a lower solubilizing efficiency than the quaternary moiety (DMAEMA·EtBr). In the latter case, higher % oleophilic (AMD-N-C_{18}) could be incorporated into the polymer chain and still maintain water solubility of the polymer.

Additionally, another type of weakly cationic amphipathic terpolymer was investigated. This involved post-reacting a nonionic AMD/AMD-N-C_{18} copolymer in aqueous solution with formaldehyde and diethylamine (Mannich reaction) as follows:



The method employed was essentially that of Schiller and Suen (2) (Ind. Eng. Chem. 48, 2132 (1956)).

The base polymer used was a 99% AMD/1% AMD-N-C_{18} copolymer. A stock solution was prepared (4.85% in water, Brookfield viscosity = 510 cps). An aliquot of this solution containing 10 gms of polymer was placed in a 500 ml reaction flask equipped with stirrer, internal thermometer, condenser, and water bath. Na_3PO_4 (1.1 gm) was added plus sufficient 10% NaOH to give a pH of 10.4. Formaldehyde (37% reagent grade) was added and the temperature held at 45 to 50°C for 90 minutes. Diethylamine (Union Carbide) was then added and the temperature increased and held at 70 to 75°C for 30 minutes. The solution was transferred to a rotary evaporator and stripped at 50

mm Hg using a 60°C bath. The pH of the solution was adjusted to 7 with 10% HCl.

Table X Weak Cationic Polymers

Sample	Mole Ratio AMD/HCHO/$HNEt_2$	% Solids	Brookfield Visc, cps	Foam Height*, mls
003-39A	1/0.1/0.1	5.67	1500	140
B	1/0.3/0.3	5.44	6400	260
C	1/0.5/0.5	6.34	600,000	290

* 0.05% polymer solution

From results in Table X it would appear that the foaming efficiency increased with increasing % cationic group. The increasing viscosity with increasing % cationic (particularly comparing B and C) is probably due to crosslinking by formaldehyde since it was observed that the solutions increased in viscosity on storage at room temperature.

Due to their instability, this approach was dropped and no further evaluation of this system was undertaken.

ANIONIC POLYMERS

The remaining polymers in this study were prepared using as the termonomers, acrylic acid (AA) and 2-sulfoethyl methacrylate (SEMA) to give the weak and strong anionic systems respectively. The thermal as well as the UV polymerizations were both found to require an additional quantity of t-butanol during the course of the polymerization reaction in order to maintain a fluid suspension. The catalyst level in the UV system for both series had to be raised to 0.15 parts phm in order to obtain good yields, above 97%. The normal concentration

of 0.1 part phm gave yields below 50%. The various polymers were characterized with respect to their Brookfield Viscosities and foam heights at pH's of 4, 6, and 8 after adjustment with NaOH.

As seen in Table XI, both the viscosity and foam heights were found to be a function of the pH. The viscosity was generally found to be the highest at a pH 4 and to decrease with increasing pH. The aqueous solutions at pH 4 were quite gelatinous and, therefore, the accuracy of the viscosity data is doubtful. The foaming tendency appears to be related to the concentration of the oleophilic moiety (AMD-N-C_{18}), increasing with increasing oleophile, as well as being pH sensitive.

The strong anionic amphipathic terpolymers were evaluated under similar conditions, Table XII. The foaming tendency was found to be relatively independent of the pH. The Brookfield viscosity, like the weak anionic system, was found to decrease with increasing pH. The UV series was found to be highly gelatinous in nature over the entire pH range indicating perhaps a high degree of hydrogen bonding.

Table XI Weak Anionic Amphipathic Polymers

Thermal Polymerization

Sample	AMD/AMD-N-C_{18}/AA	pH	% Solids	Visc. cps	Foam Height, mls*
003-47A	67/3/30	4.0	---	-----	---
B	57/3/40	4.0	.85	6,700	240
C	66/4/30	4.0	.82	8,000	250
D	56/4/40	4.0	.96	20,000	150
E	65/5/30	4.0	.92	7,000	350
F	55/5/40	4.0	.88	5,000	200
003-47A	67/3/30	6.0	.96	35	80
B	57/3/40	6.0	.92	34	50
C	66/4/30	6.0	.82	63	250
D	56/4/40	6.0	.99	74	75
E	65/5/30	6.0	.93	1,875	325
F	55/5/40	6.0	.89	620	175
003-47A	67/3/30	8.0	.94	30	60
B	57/3/40	8.0	.96	25	35
C	66/4/30	8.0	.91	50	150
D	56/4/40	8.0	.94	50	35
E	65/5/30	8.0	1.1	108	250
F	55/5/40	8.0	.79	106	150

UV Polymerization

003-56A	67/3/30	4.0	0.96	7,000	100
B	57/3/40	4.0	0.92	2,400	75
C	66/4/30	4.0	1.24	14,000	45
D	56/4/40	4.0	1.12	12,000	60
E	65/5/30	4.0	0.76	14,000	70
F	55/5/40	4.0	0.91	11,000	60
003-56A	67/3/30	6.0	0.91	1,175	110
B	57/3/40	6.0	0.92	210	75
C	66/4/30	6.0	0.83	7,900	225
D	56/4/40	6.0	0.92	400	110
E	65/5/30	6.0	0.99	60,000	100
F	55/5/40	6.0	0.95	79,000	115
003-56A	67/3/30	8.0	0.90	100	20
B	57/3/40	8.0	0.98	160	60
C	66/4/30	8.0	0.92	88	60
D	56/4/40	8.0	1.04	122	75
E	65/5/30	8.0	0.95	13,000	200
F	55/5/40	8.0	0.95	1,450	190

*0.05% polymer solution

Table XII Strong Anionic Amphipathic Polymers

Thermal Polymerization

Sample	AMD/AMD-N-C_{18}/SEMA	pH	% Solids	Visc, cps	Foam Height, mls*
003-55A	67/3/30	2.5	.89	2,000	340
B	57/3/40	2.5	.99	2,100	360
C	66/4/30	2.5	.99	7,600	180
D	56/4/40	2.5	.99	230	100
E	65/5/30	2.5	.96	210	10
F	55/5/40	2.5	.97	1,360	20
003-55A	67/3/30	4.0	.96	900	400
B	57/3/40	4.0	.99	815	350
C	66/4/30	4.0	.98	5,000	200
D	56/4/40	4.0	.98	200	75
E	65/5/30	4.0	.95	175	10
F	55/5/40	4.0	.96	2,250	40
003-55A	67/3/30	6.0	.96	400	375
B	57/3/40	6.0	.93	420	280
C	66/4/30	6.0	.95	2,450	180
D	56/4/40	6.0	.92	90	90
E	65/5/30	6.0	.96	80	10
F	55/5/40	6.0	.96	1,750	35
003-55A	67/3/30	8.0	.95	340	250
B	57/3/40	8.0	.94	400	275
C	66/4/30	8.0	.94	2,250	150
D	56/4/40	8.0	.96	88	110
E	65/5/30	8.0	.92	75	15
F	55/5/40	8.0	.93	650	40

UV Polymerization

003-57A	67/3/30	3.0	.93	15,000	25
B	66/4/30	3.0	.89	13,000	100
C	56/4/40	3.0	.96	18,500	10
D	65/5/30	3.0	.85	31,000	---
003-57A	67/3/30	6.0	.95	8.700	75
B	66/4/30	6.0	1.13	2,700	125
C	56/4/40	6.0	.94	8,200	25
D	65/5/30	6.0	.87	17,000	40
003-57A	67/3/30	8.0	.94	7,800	125
B	66/4/30	8.0	.91	2,400	80
C	56/4/40	8.0	1.07	7,200	20
D	65/5/30	8.0	1.01	15,500	25

*0.05% polymer solution

EXPERIMENTAL - EVALUATION

Unsettled raw sewage was obtained from Camden-Wyoming, Delaware and from Smyrna, Delaware. These communities were selected because they are mostly residential without the complications of industrial waste. Fifteen gallons of raw sewage was collected at approximately the same time each morning (8:30 AM at Camden-Wyoming and 9:00 AM at Smyrna). The time was selected in order to sample the maximum morning flow of sanitary waste.

Early experiments with settled primary sewage were disappointing. The polymer-flotation process appears to work best with high-solids waste water.

Substantial changes in the sewage being fed to the experimental units during the 2 to 4 hours duration of the test were observed. Slight agitation of the storage tank reduced the change to an acceptable level. Agitation-induced coagulation of the solids was obtained with even moderate agitation.

CONTINUOUS FLOTATION CELL

First polymer evaluations were conducted in a continuous flotation cell similar to that employed by Grieves and Crandall [3] and Rubin, et al [4]. The final test unit was modified many times before reaching its current configuration (Figures 1 and 2).

Bubble size, recirculation rate, and the division between overflow and "product" produced were the major control factors. The air flow was controlled by a Cartesian Diver type of absolute pressure control and was measured with a manometer and flowmeter.

This air stream was divided between two matched 30 to 40 micron polyethylene filter candles. Additional filter candles were tried, but proved to be difficult to adjust and did not appear to aid the separation.

Several variations in recirculation rate and pattern within the flotation cell were investigated. The most effective separation was achieved using equal areas for the inner cylinder and the outer ring. The location of the "product" outlet was not critical. Almost any point on the downward circulation ring was satisfactory. A 9 to 1 ratio between product and overflow was selected as being realistic and controllable in the small volumes being employed. Lower overflow rates increased the recirculation of the foam-solids causing plugging of the monitoring equipment, especially the 10mm x 10mm flow-thru cell used for % transmission.

Temperature of the influent did not vary more than $\pm$ 3°C and that variation had no detectable effect on the process evaluation. Total flow to the flotation cell was 500 ml./min., equivalent to 0.935 gpm/ft^2 of surface area, a value arbitrarily selected to minimize the sewage needed per test.

It was most cumbersome to monitor a continuous cell with conventional suspended solids determinations. A Beckman D. K. 2A Spectrophotometer, utilizing a flow-thru cell for the "product" and a static cell filled with distilled water for comparison, was employed to continuously monitor the flotation process. Samples for suspended solids [5] were taken at regular intervals for correlation

with the Beckman % Transmission @ 530 mu. No correlation was observed (Table XIII).

Continuously removing the accumulated foam from the surface minimized its recycle and improved the separation efficiency. Foam volume is not necessarily indicative of the polymers effectiveness, nor is the foam height in the standard lab test in distilled water (Table XIII). Grieves, et al [6] report that bacteria will reduce the foaming capacity of surface active substances. The high bacterial content in raw sewage may therefore have a major effect on foam generation.

The flotation cell was run each day to maximum % transmission without addition of polymer, reported in Table XIII, Column 1. When equilibration (as measured by constant % Transmission) was reached, the polymer solution was metered into the raw sewage just before it entered the cell. Thus, the polymer dosage was continuously increasing until the test was completed. The maximum % transmission attained and the corresponding polymer dosage (by calculation) is reported in Table XIII, Column 2. The instantaneous polymer dosage was determined by calculation.

"Standard" test conditions for the continuous flotation cell were:

Raw sewage flow rate	-	500 ml./min.
"Product" " "	-	450 " "
Overflow " "	-	50 " "
Temperature	-	17.5 $\pm$ 3°C
Air flow rate	-	240 ml./min.
Air pressure	-	2.0 cm. Hg.
Polymer feed rate	-	1.85 ml./min.

TABLE XIII

FLOCCULATION OF RAW SEWAGE - AMPHIPATHIC POLYMERS

	Polymer Sample	Approx. Dosage* PPM	% Transmission @ 530 mu		Suspended Solids, mg/l			Foam Hgt., mls.
			Raw (1)	Treated (2)	Raw Sewage	Raw Sewage in unit, untreated (3)	Treated (4)	
NONIONIC (Thermally Initiated)	003-18A	19	30	34	220	232	230	225
	-18B	24	38	41	104	52	48	150
	-18C	28	35	36	64	28	36	100
	-18D	34	36	38	116	124	60	70
	-18D	46	36	40	---	---	---	---
NONIONIC (U. V. Initiated)	003-34A	19	30	34	172	140	156	270
	-34B	34	47	51	124	100	96	365
STRONGLY CATIONIC (No Oleophile, Thermally Initiated)	003-52A	9	45	47	228	200	224	0
	-52B	22	57	60	44	24	16	0
	-52B	47	57	63	---	---	---	---
	-52D	24	51	65	56	44	32	0
	-52D	31	51	68	---	---	---	---
	-52E	28	41	41	---	---	---	---
	-52E	>100	41	55	108	96	68	0
STRONGLY CATIONIC (Thermally Initiated)	003-20A	23	32	38	---	---	---	100
	-20A	54	32	50	---	---	---	---
	-20B	34	32	48	---	---	---	50
	-20C	49	40	61	136	---	40	60
	-20D	40	33	40	156	152	112	185
	-20D	>100	33	46	---	---	---	---
	-20E	28	34	58	144	168	48	300
	-20F	34	38	53	248	224	188	500

*This dosage level corresponds to the maximum % Transmission obtained by gradually increasing dosage during continuous operation.

Columns (1) and (2) correspond to columns (3) and (4) respectively showing changes in % Transmission and suspended solids attributable to the flotation process.

TABLE XIII - Contd.

FLOCCULATION OF RAW SEWAGE - AMPHIPATHIC POLYMERS

	Polymer Sample	Approx. Dosage* PPM	% Transmission @ 530 mu		Suspended Solids, mg/l			
			Raw (1)	Treated (2)	Raw Sewage	Raw Sewage in unit, untreated (3)	Treated (4)	Foam Hgt., mls.
STRONGLY	003-45A	24	32	49	156	84	8	0
CATIONIC	-45A	>100	32	67	---	---	---	---
(U. V. Ini-	-45B	28	21	41	224	236	88	0
tiated)	-45B	>100	21	72	---	---	---	---
	-45C	28	22	38	168	120	52	0
	-45C	46	21	61	---	---	---	---
	-45D	24	44	50	136	124	92	85
	-45D	47	44	63	---	---	---	---
	-45E	21	41	46	116	96	40	180
	-45E	>100	41	63	---	---	---	---
WEAKLY	003-41A	19	44	48	76	40	20	305
CATIONIC	-41A	>100	44	50	---	---	---	---
(Thermally	-41B	34	44	47	68	24	8	236
Initiated)	-41B	>100	44	62	---	---	---	---
	-41C	28	45	49	200	192	144	425
	-41C	42	45	65	---	---	---	---
	-41D	50	45	67	160	142	124	425
	-41E	24	50	71	108	112	40	475
	-41F	19	52	76	132	124	44	425
WEAKLY	003-47A	9	41	41	112	96	96	80
ANIONIC	-47B	5	47	47	64	72	44	50
(Thermally	-47C	13	47	48	120	96	100	250
Initiated)	-47D	5	52	53	---	---	---	75

*This dosage level corresponds to the maximum % Transmission obtained by gradually increasing dosage during continuous operation.

Columns (1) and (2) correspond to columns (3) and (4) respectively showing changes in % Transmission and suspended solids attributable to the flotation process.

The "Product" was evaluated by measuring total suspended matter and % Transmission at 530 mu.

One or more examples of each class of polymer were tested in the continuous flotation cell. The cationic polymers were the only effective types. Polymer dosage/performance curves for the more effective classes are shown in Figures 3 through 6.

PRESSURIZED WATER FLOTATION

The Robert A. Taft Sanitary Engineering Laboratory kindly loaned us a pressurized water flotation unit (Figure 7). Distilled water was pressurized with air at about 60 p.s.i.g. in a copper cylinder. This pressurized water was introduced into the bottom of the transparent test chamber. Very fine bubbles were formed, much like a freshly uncapped soda bottle. This equipment proved to be convenient to operate and quite efficient in removing solids without polymer treatment.

Agitation of the sewage prior to polymer addition had little effect upon the test. The rate of polymer addition also had little effect upon test results. The rate of pressurized water addition was quite important as would be expected. A nominal 500 ml of pressurized water in 1 min. was selected as being reproducible though not necessarily optimum.

The "standard" test procedure for the pressurized water flotation unit was: Agitate 1000 ml. raw sewage 2 min., add polymer as a 0.1% solution, agitate 2 min., add 500 ml. pressurized water in 1 min., allow to stand 2 min. and take sample for turbidity

measureme t (Beckman % Tr: ismission @ 530 mu). It should be noted that this procedure results in dilutions of 1 liter of sewage to 1.5 liters and % transmissions will thus increase even though no solids are removed. The effectiveness of a polymer must therefore be judged against a "floated sewage" blank in which no polymer is added rather than against the raw sewage.

All polymers were evaluated by this rapid test (Figures 8 through 17). As with the continuous flotation cell, the cationic polymers were the most effective. A commercially available cationic polymer [7] was included in each test set to aid in comparing performance on differing samples of sewage.

JAR TESTING

Conventional jar testing was employed to relate the continuous flotation cell and the pressurized water flotation cell to coagulation/settling examination methods.

The "standard" test procedure for jar testing was: add polymer as 0.1% solution, agitate rapidly @ 100 rpm for 3 min., mix slowly @ 25-30 rpm for 10 min., settle for 10 min. @ 3-5 rpm, and take sample from mid-depth of the beaker for turbidity measurement.

Two of the more effective polymer series were chosen for jar testing along with several commercially available cationic flocculants (Figures 18 through 20).

COMPARISON OF EVALUATION METHODS

To aid the comparison of polymer performance as determined by the three evaluation techniques, two large lots of raw sewage were

employed to test two polymers by the three methods (Figures 21 and 22).

The pressurized water cell is the most efficient solids removal method, followed by jar testing and continuous flotation. As testing methods they seem to compare well. However, the continuous flotation cell is too cumbersome to be of real value. The pressurized water cell appears to be a rapid, effective test and correlates well with both continuous flotation and jar testing.

DISCUSSION

The nonionic and anionic (strong and weak) amphipathic polymers prepared during this investigation showed little or no flocculating ability. Only the cationic (strong and weak) amphipathic polymers demonstrated flocculating ability.

Jar testing of the strongly cationic amphipathic polymers showed an increasing flocculating efficiency with increasing per cent of the cationic comonomer (Figure 18). However, at the dosage levels (20 ppm and above) necessary to reduce suspend solids substantially, they do not appear economic. If higher molecular weights had been achieved by the preparative methods, greater effectiveness would have been expected.

The introduction of the oleophilic moiety (N-n-octadecyl acrylamide) into these polymers did produce a foaming action. Surface tension measurements showed that these amphipathic polymers associate to form quasi-micelles. Tests using continuous flotation indicate that the presence of the oleophile moiety in the cationic amphipathic polymers improved flocculating ability. Compare Figures 3, 4, and 5 (amphipathic cationic polymers) with Figure 6 (strongly cationic polymer containing no oleophile). Again, using pressurized water flotation, the amphipathic cationic polymers showed flocculating ability (Figures 9, 11, and 13) while the non-amphipathic, strongly cationic polymers showed little or none (Figure 14). However, one should be cautious in making any firm conclusion since even a low molecular weight acrylamide/DMAEMA·EtBr copolymer would be expected to demonstrate some flocculating activity. In view of the variability of domestic wastewater considerably more testing would be necessary before firm conclusions could be drawn.

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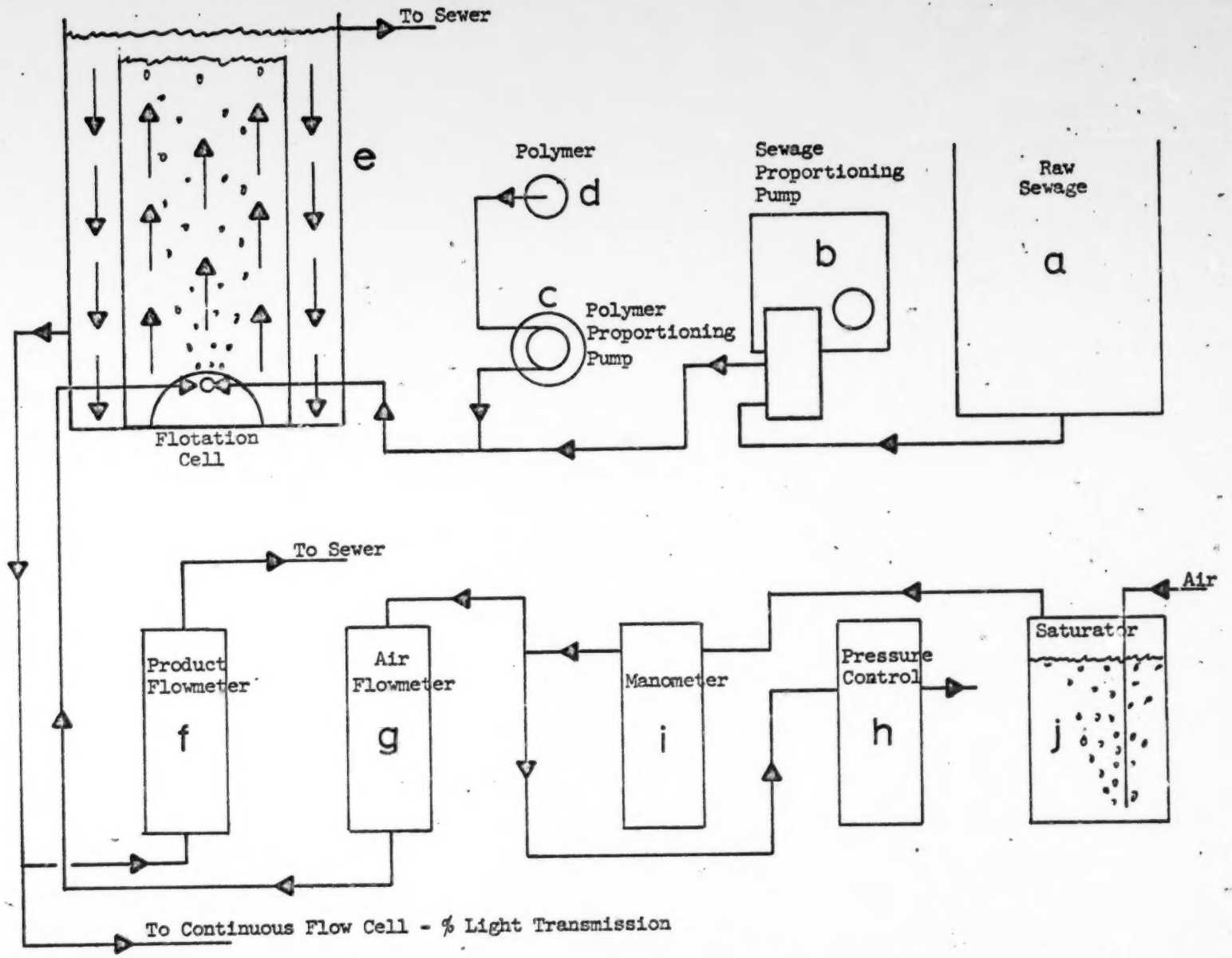

FIGURE 1. CONTINUOUS FLOTATION CELL SCHEMATIC

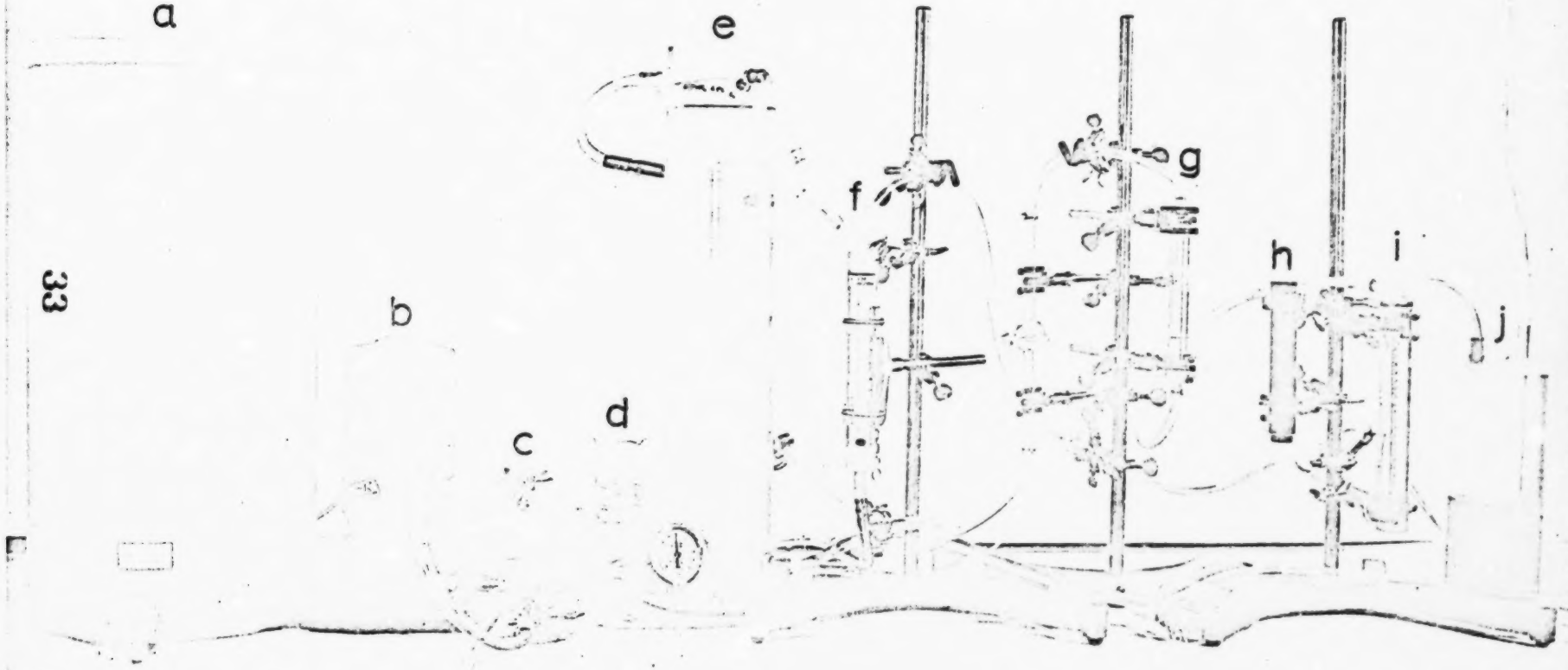

FIGURE 2. CONTINUOUS FLOTATION CELL

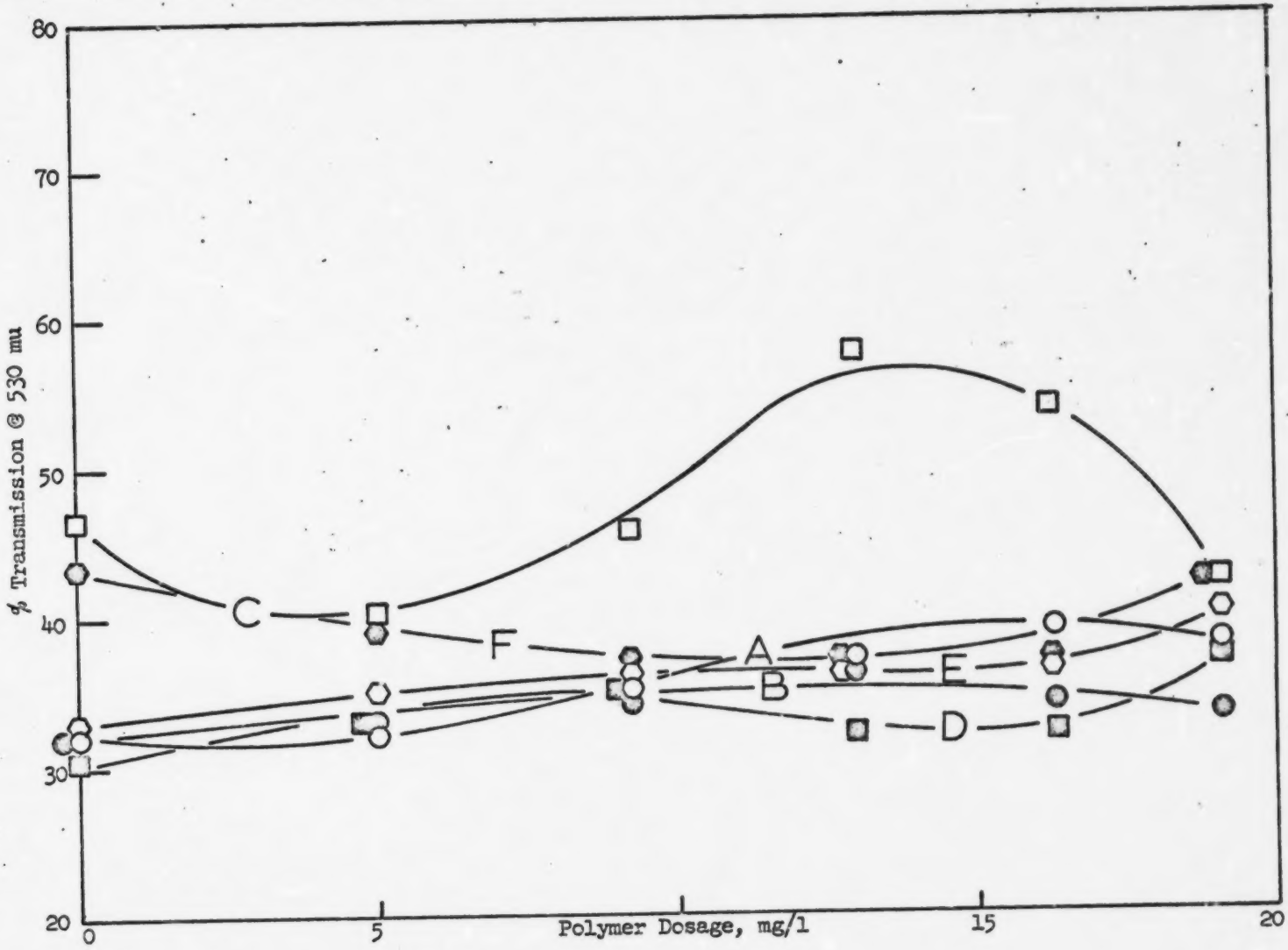

FIGURE 3. FLOTATION UNIT - POLYMERS #003-20A,B,C,D,E,F

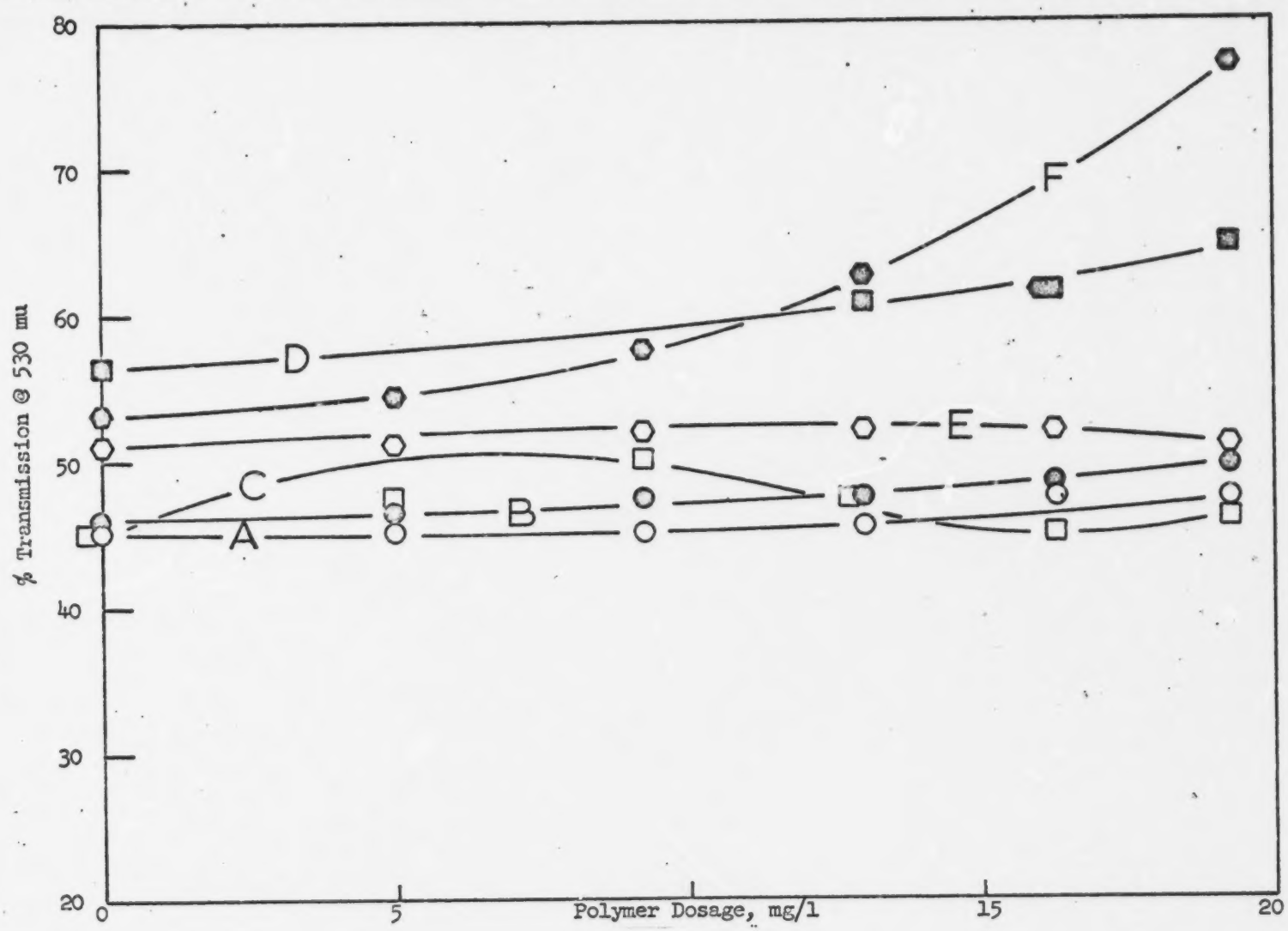

FIGURE 4. FLOTATION UNIT - POLYMERS #003-41A,B,C,D,E,F

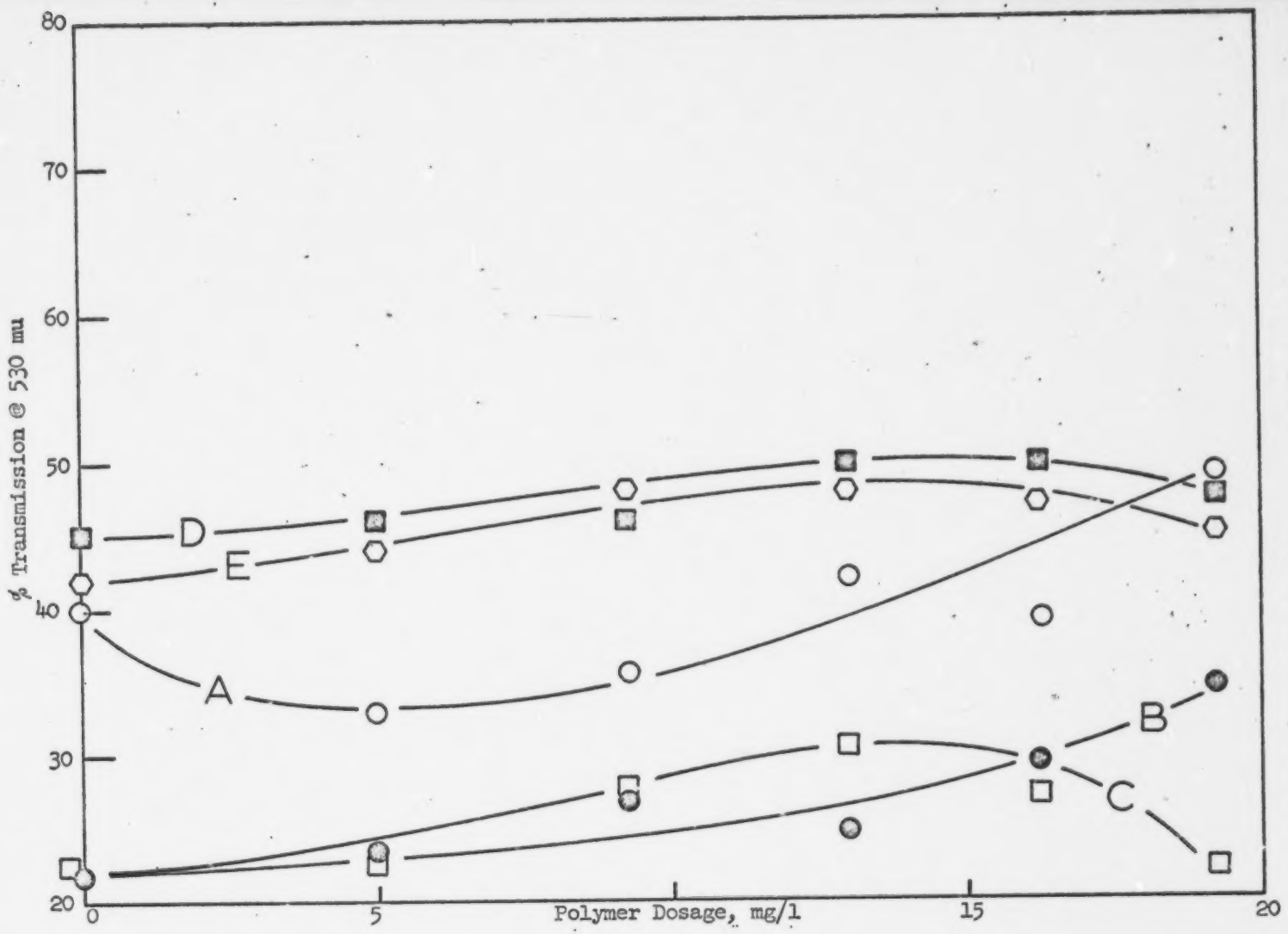

FIGURE 5. FLOTATION UNIT - POLYMERS #003-45A,B,C,D,E

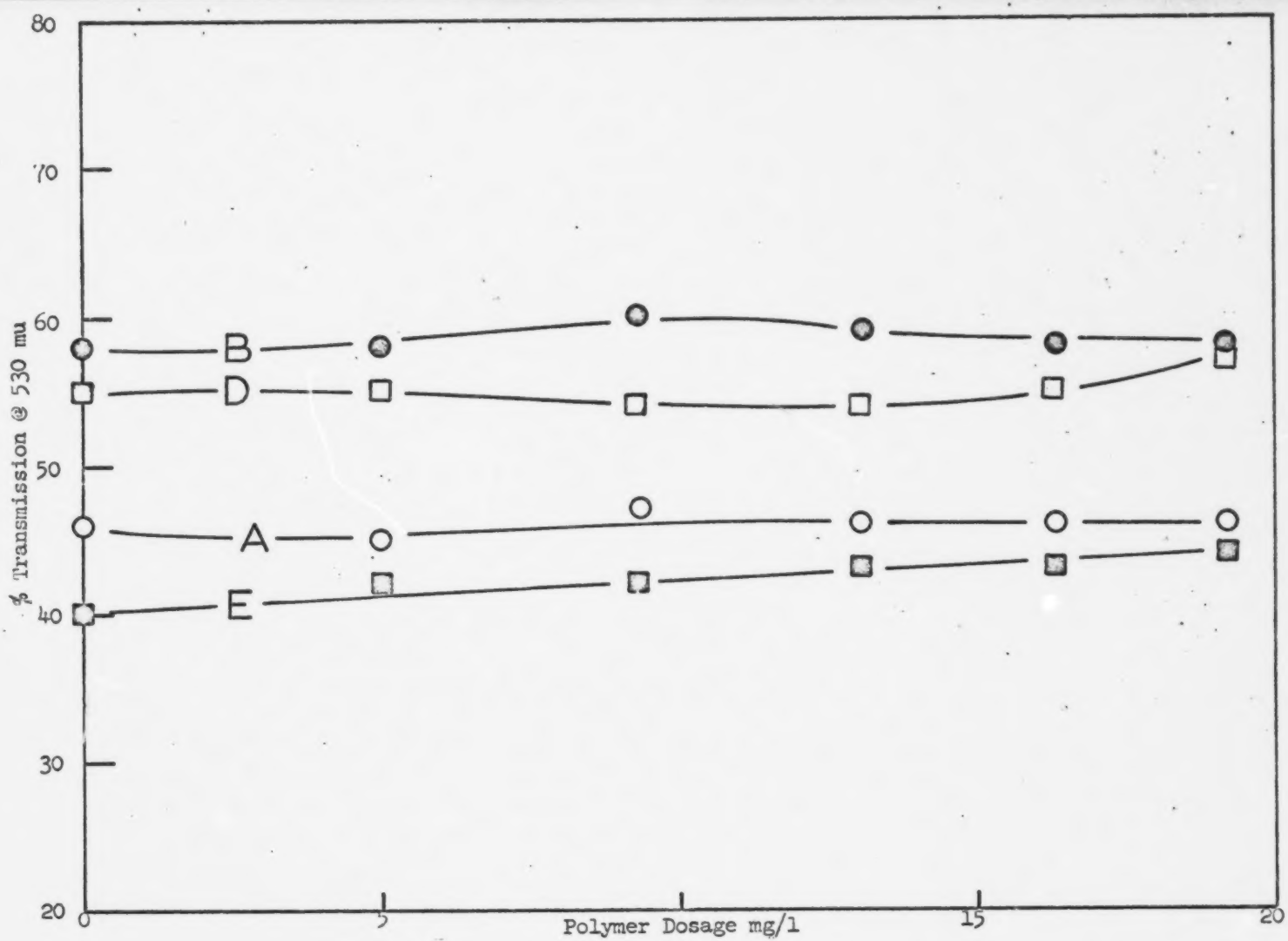

FIGURE 6. FLOTATION UNIT - POLYMERS #003-52A,B,D,E

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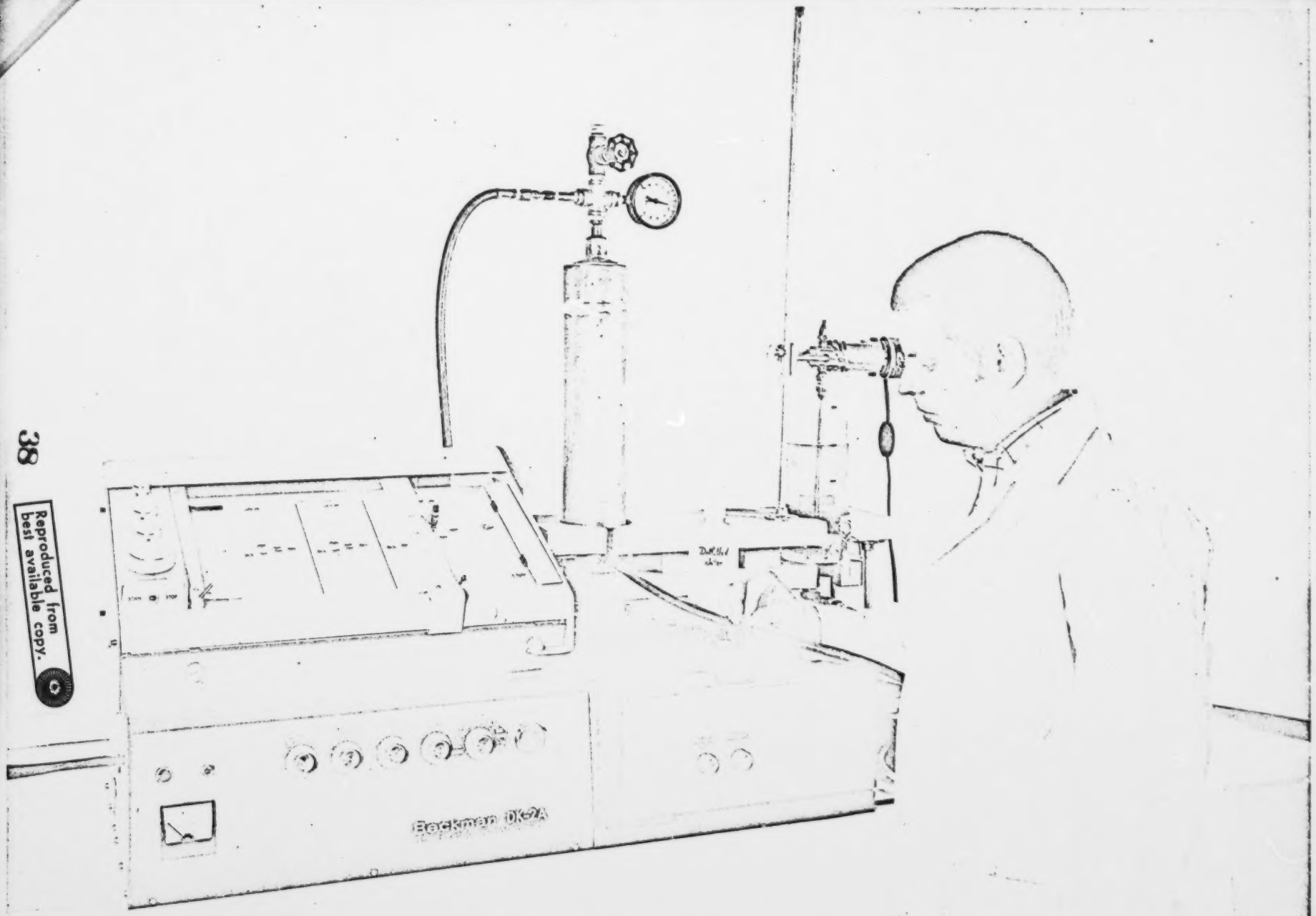

FIGURE 7. PRESSURIZED WATER FLOTATION CELL

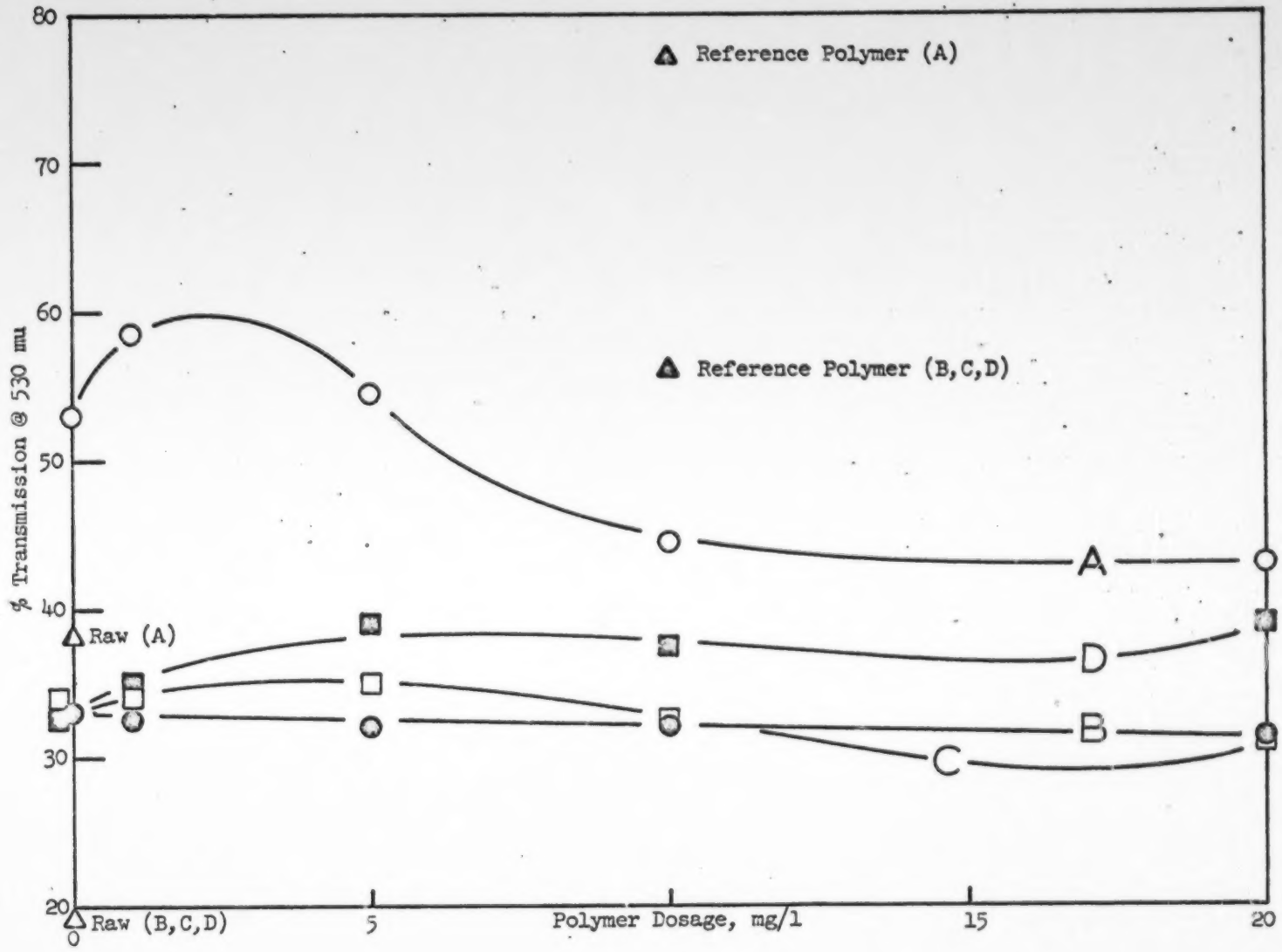

FIGURE 8. PRESSURIZED WATER - POLYMERS #003-18A,B,C,D

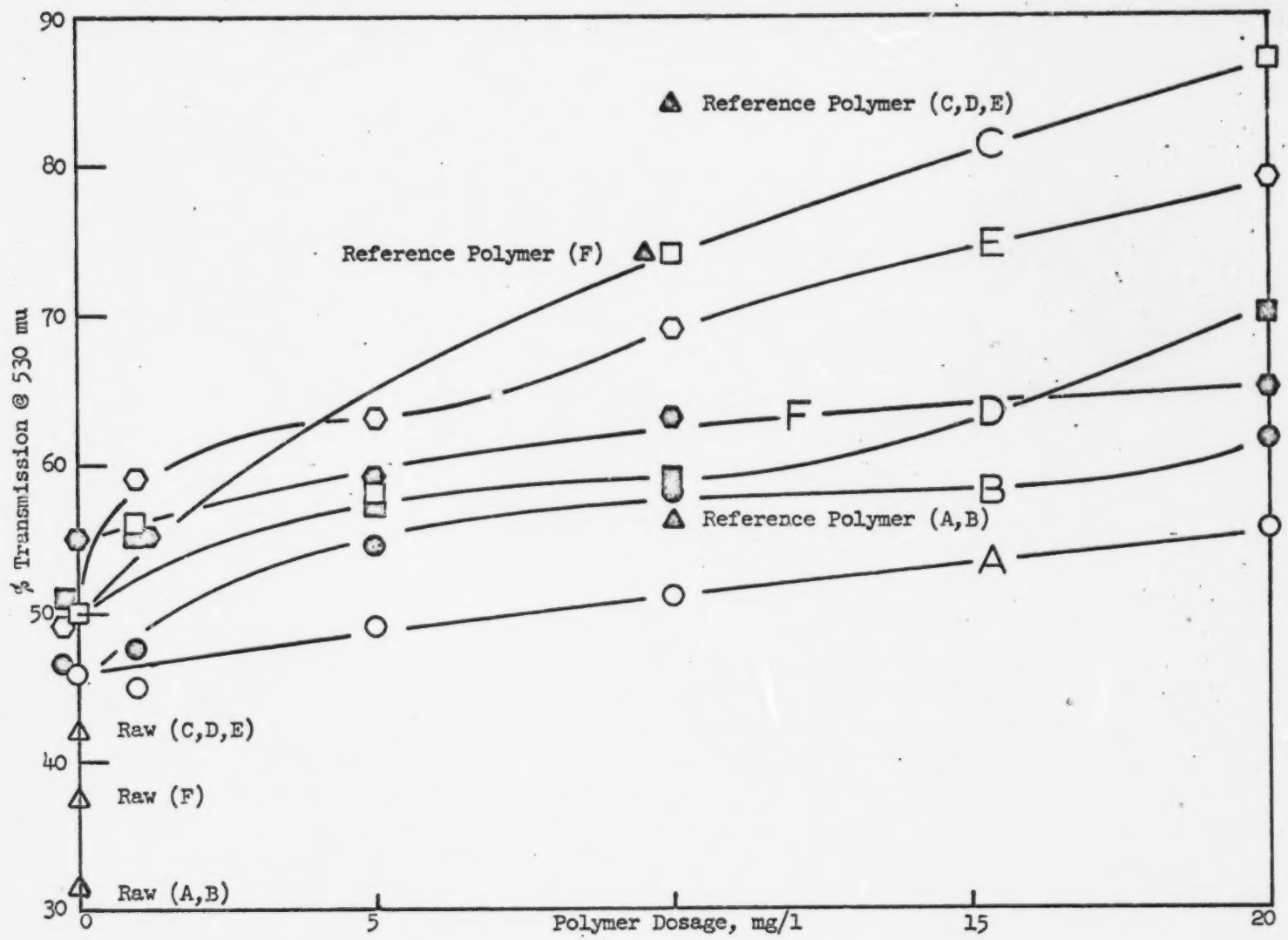

FIGURE 9. PRESSURIZED WATER - POLYMERS #003-20A,B,C,D,E,F

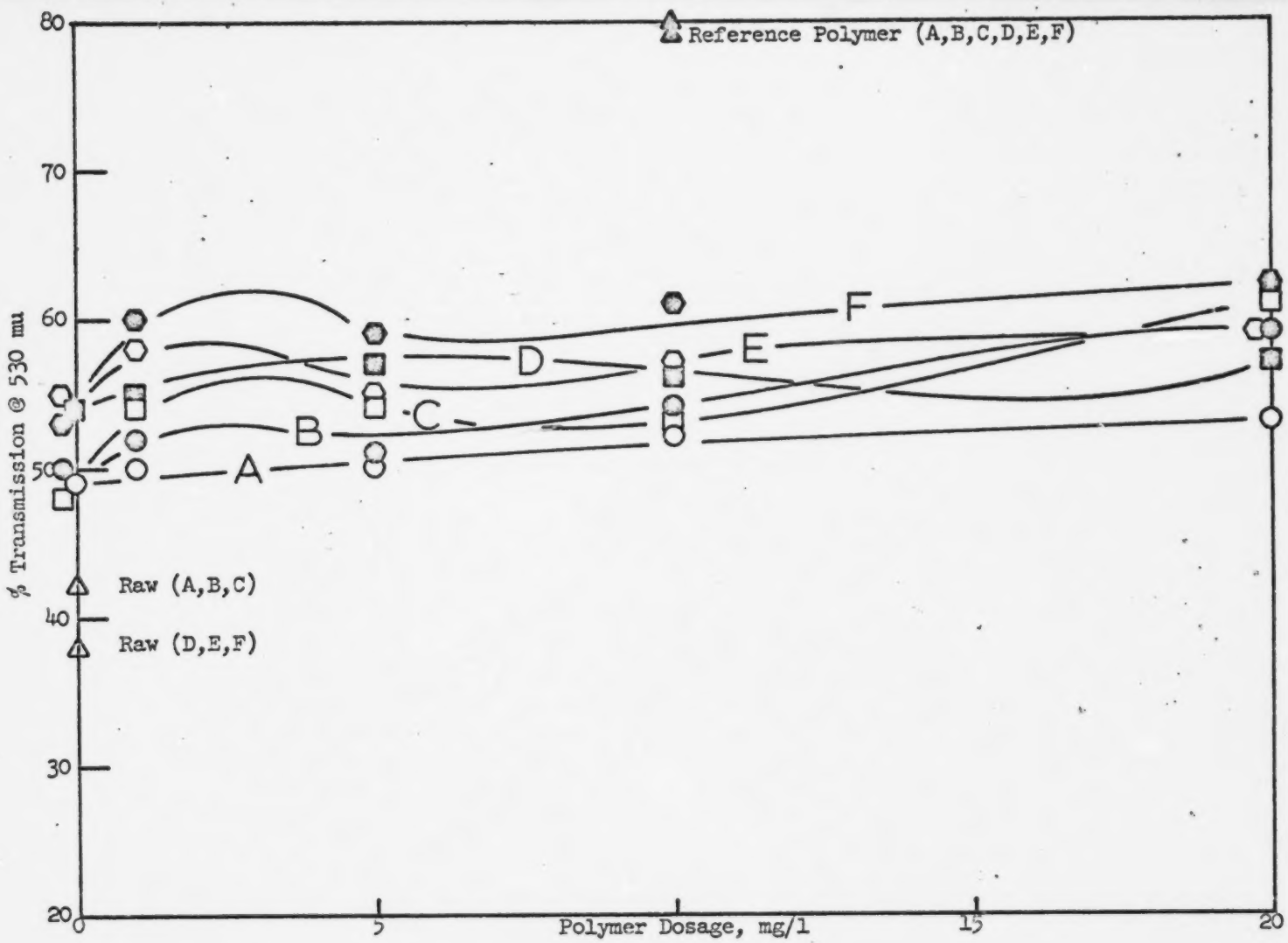

FIGURE 10. PRESSURIZED WATER - POLYMERS #003-41A,B,C,D,E,F

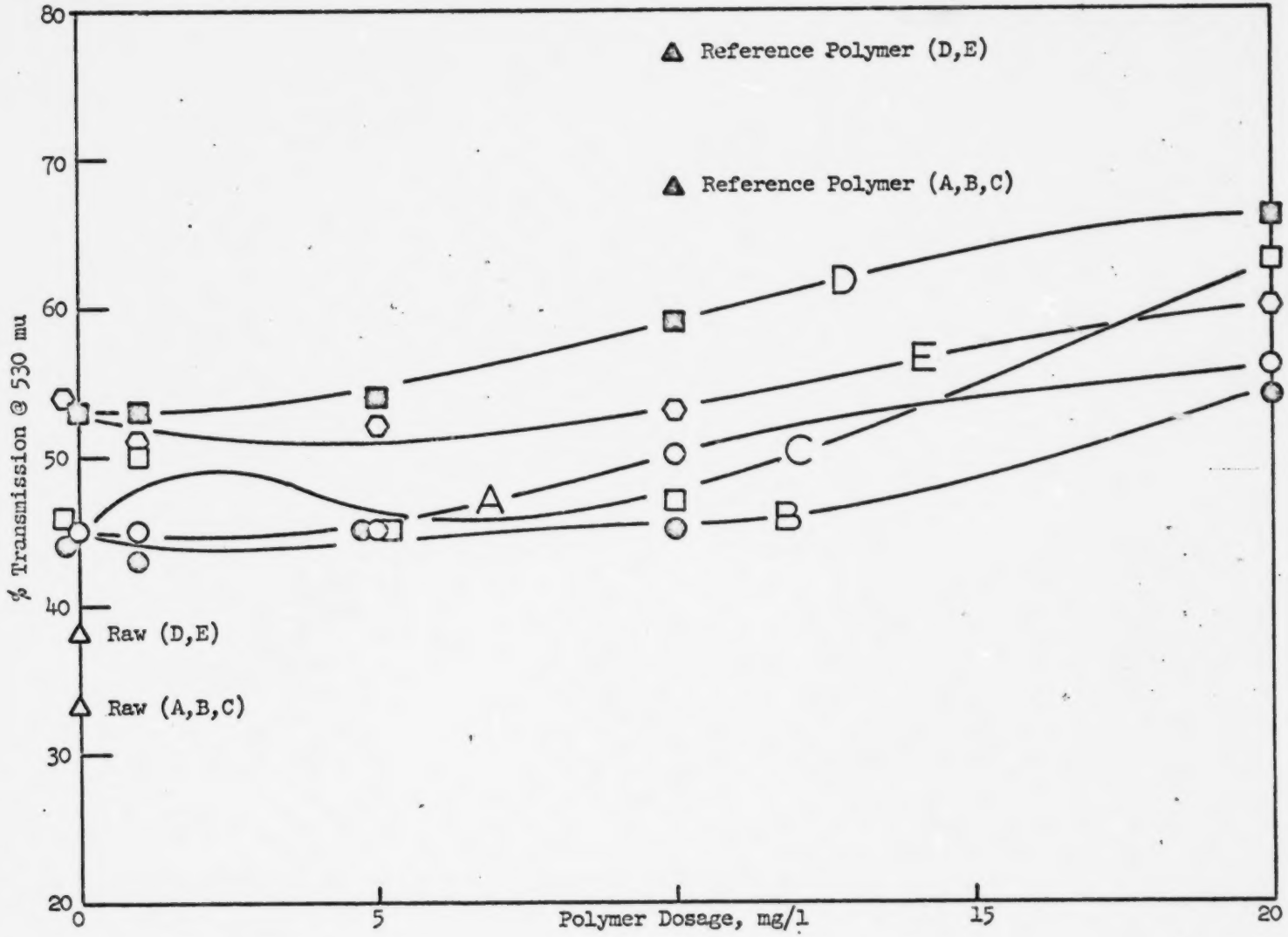

FIGURE 11. PRESSURIZED WATER - POLYMERS #003-45A,B,C,D,E

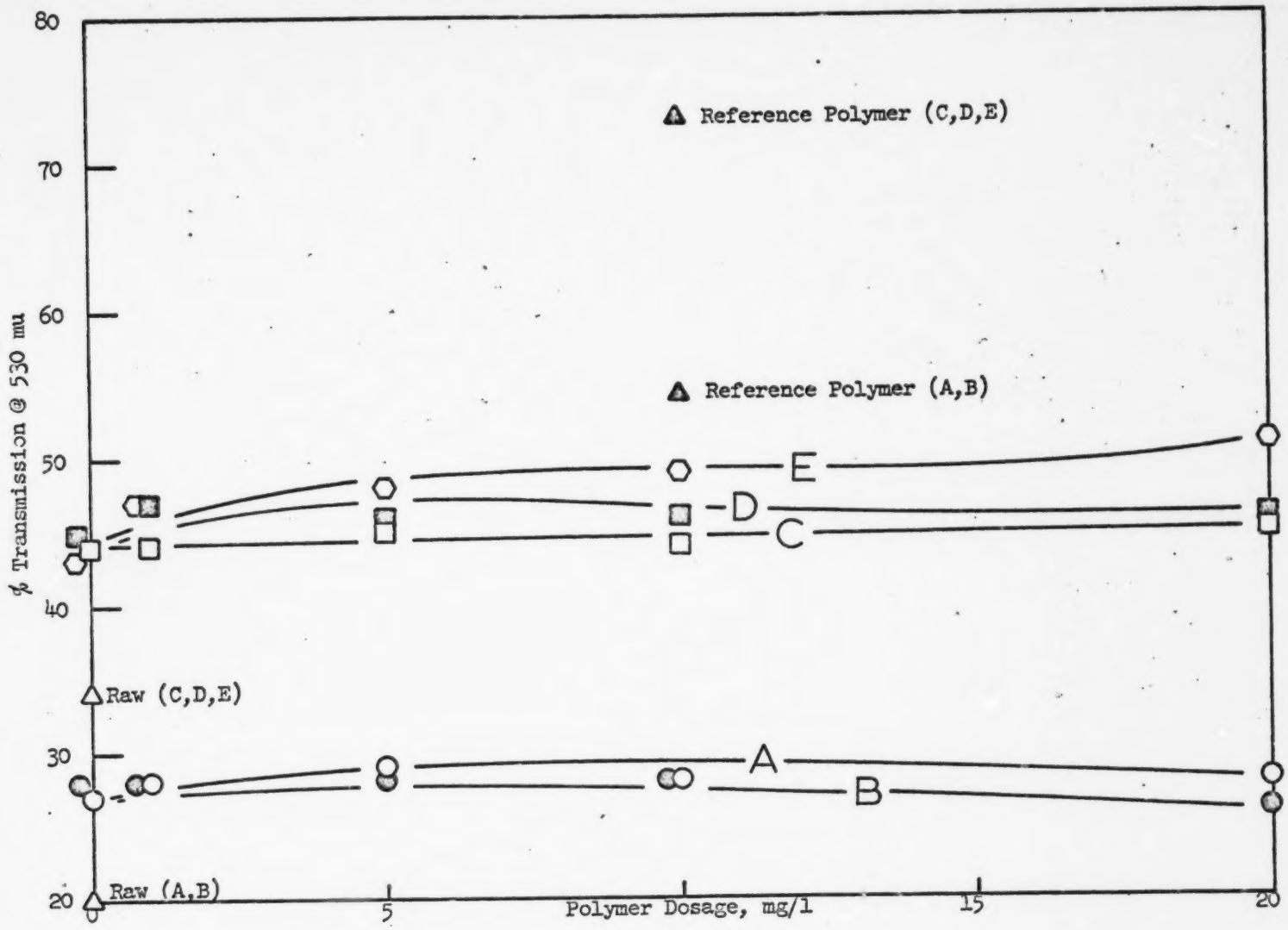

FIGURE 12. PRESSURIZED WATER - POLYMERS #003-47A,B,C,D,E

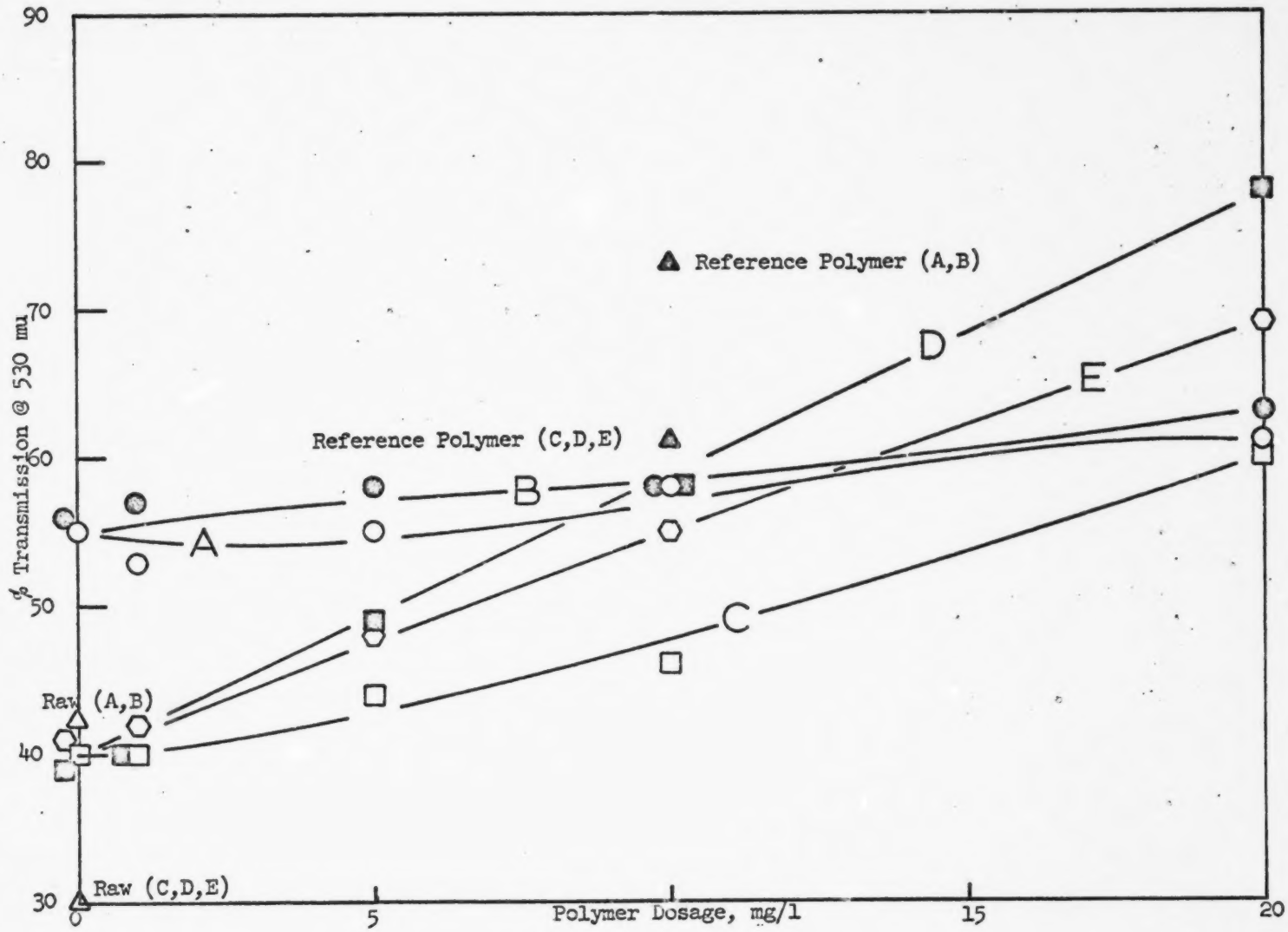

FIGURE 13. PRESSURIZED WATER - POLYMERS #003-51A,B,C,D,E

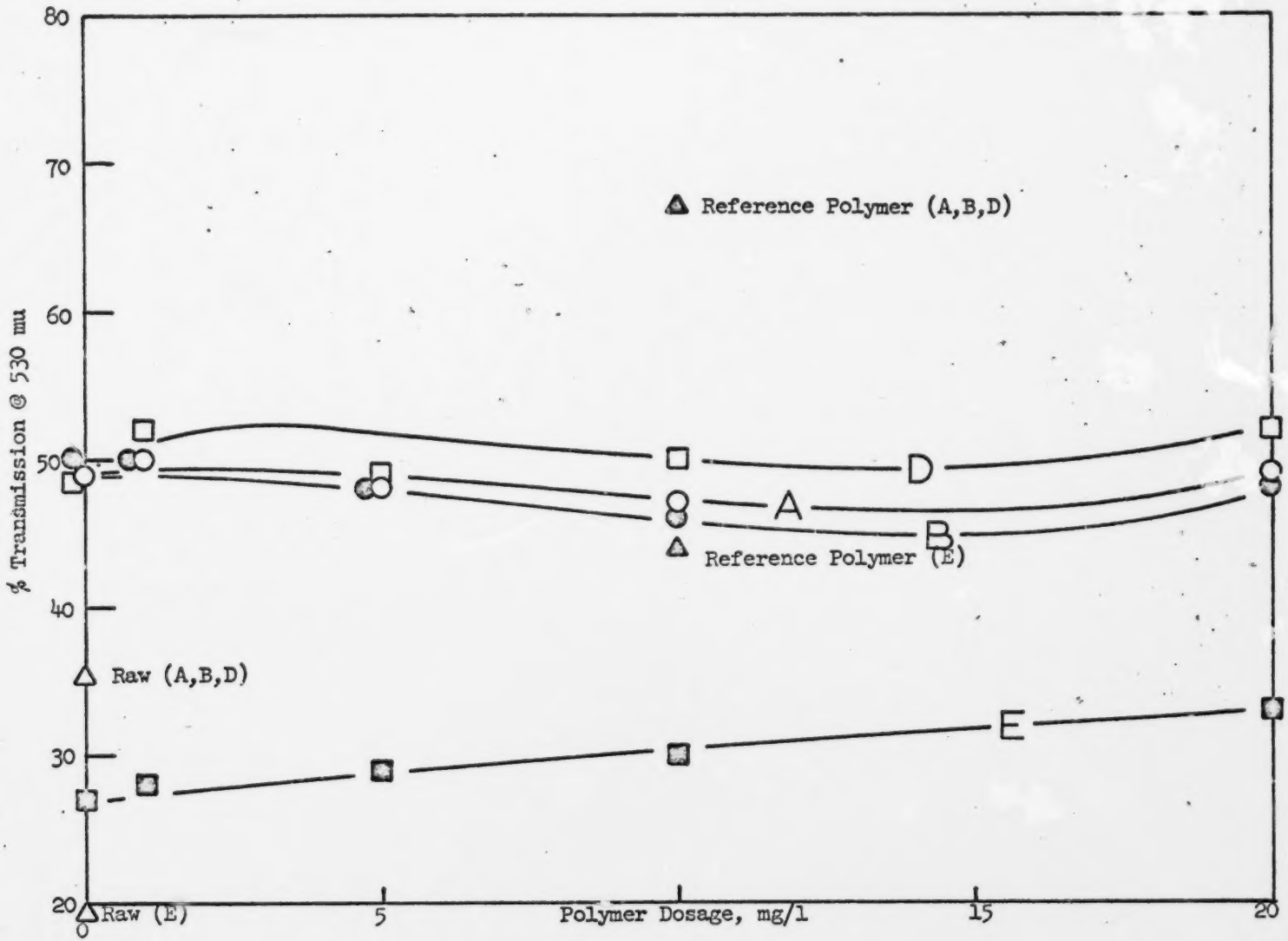

FIGURE 14. PRESSURIZED WATER - POLYMERS #003-52A,B,D,E

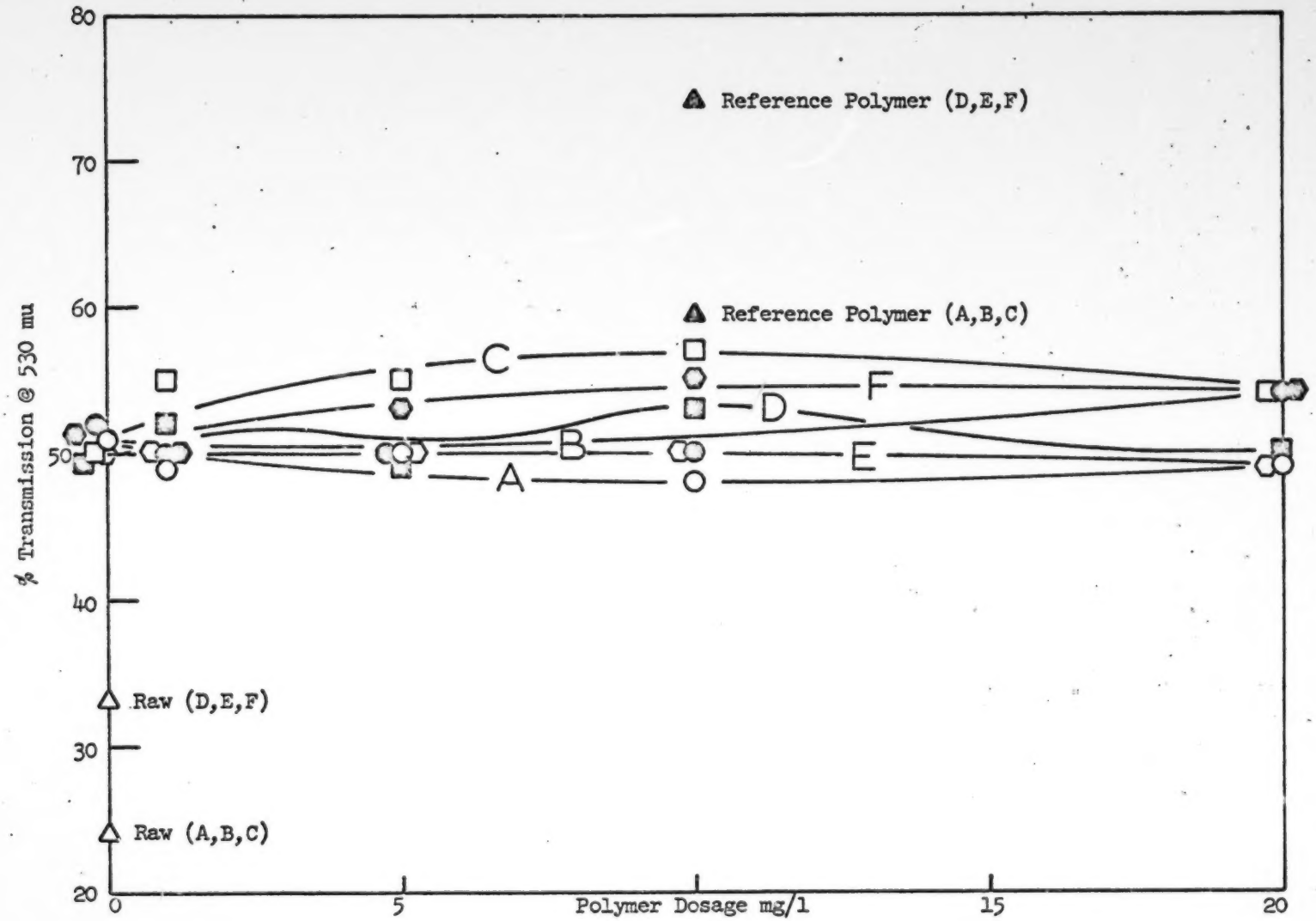

FIGURE 15. PRESSURIZED WATER - POLYMERS #003-55A,B,C,D,E,F

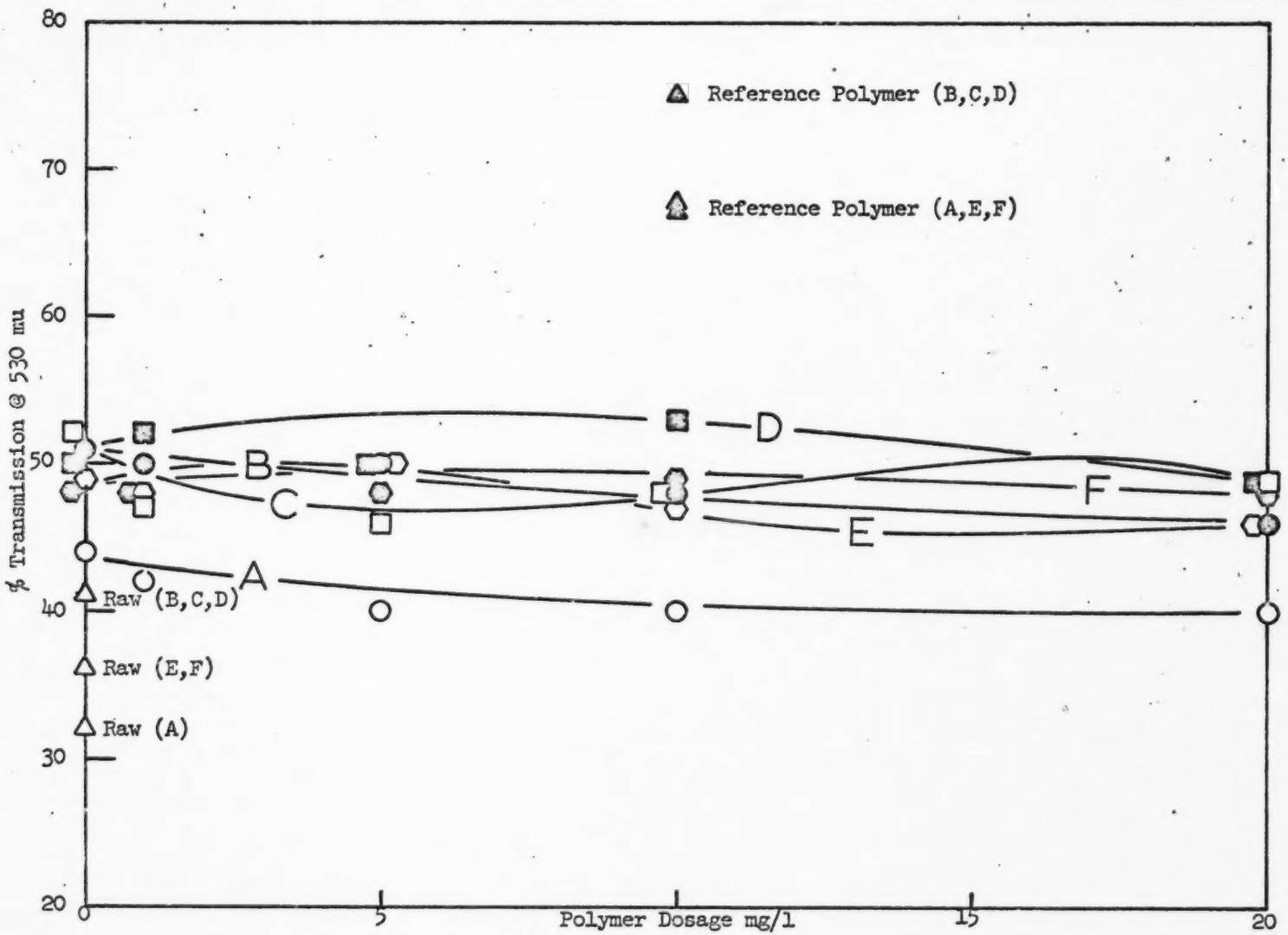

FIGURE 16. PRESSURIZED WATER POLYMERS #003-56A,B,C,D,E,F

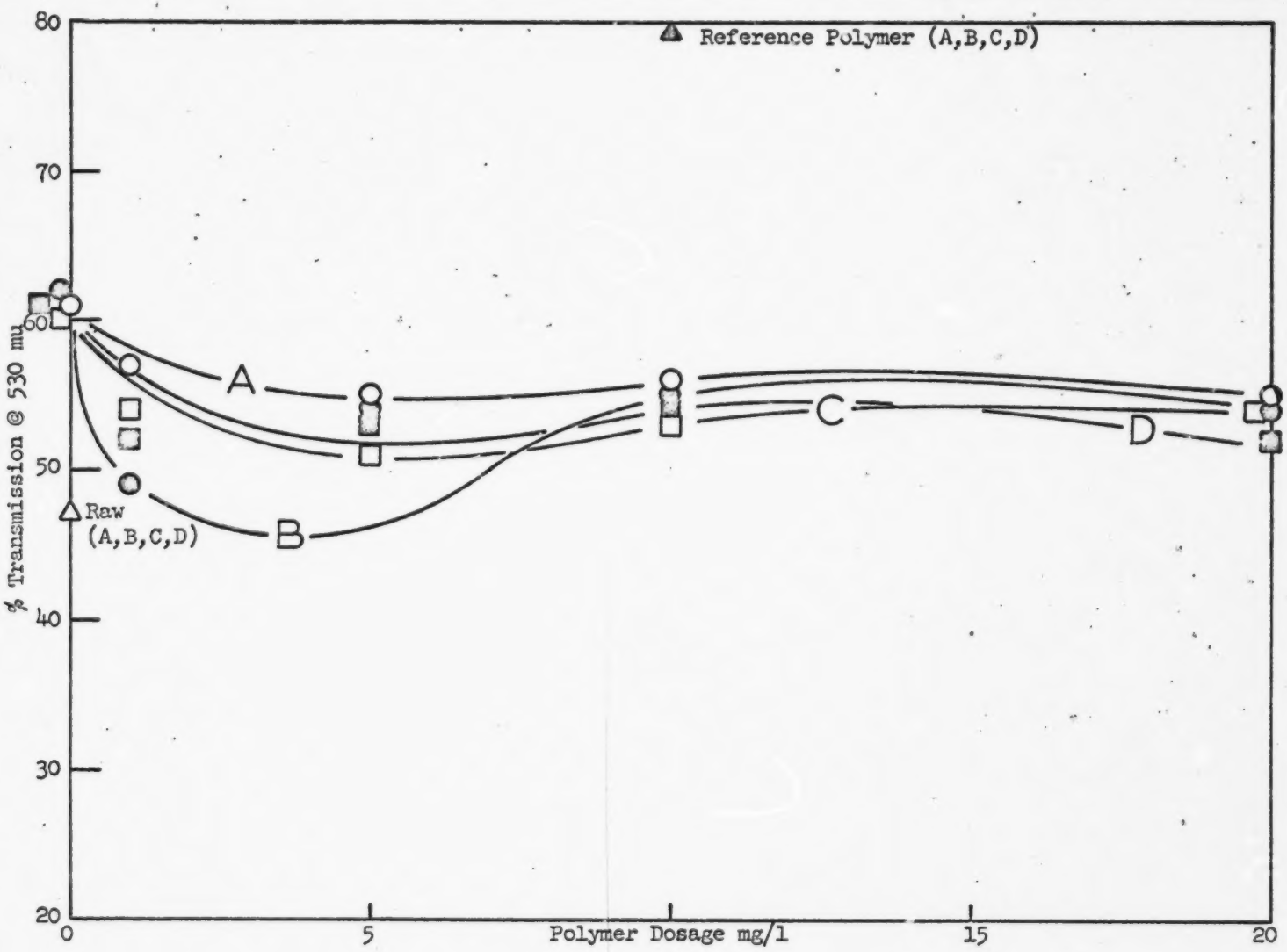

FIGURE 17. PRESSURIZED WATER POLYMERS #003-57A,B,C,D

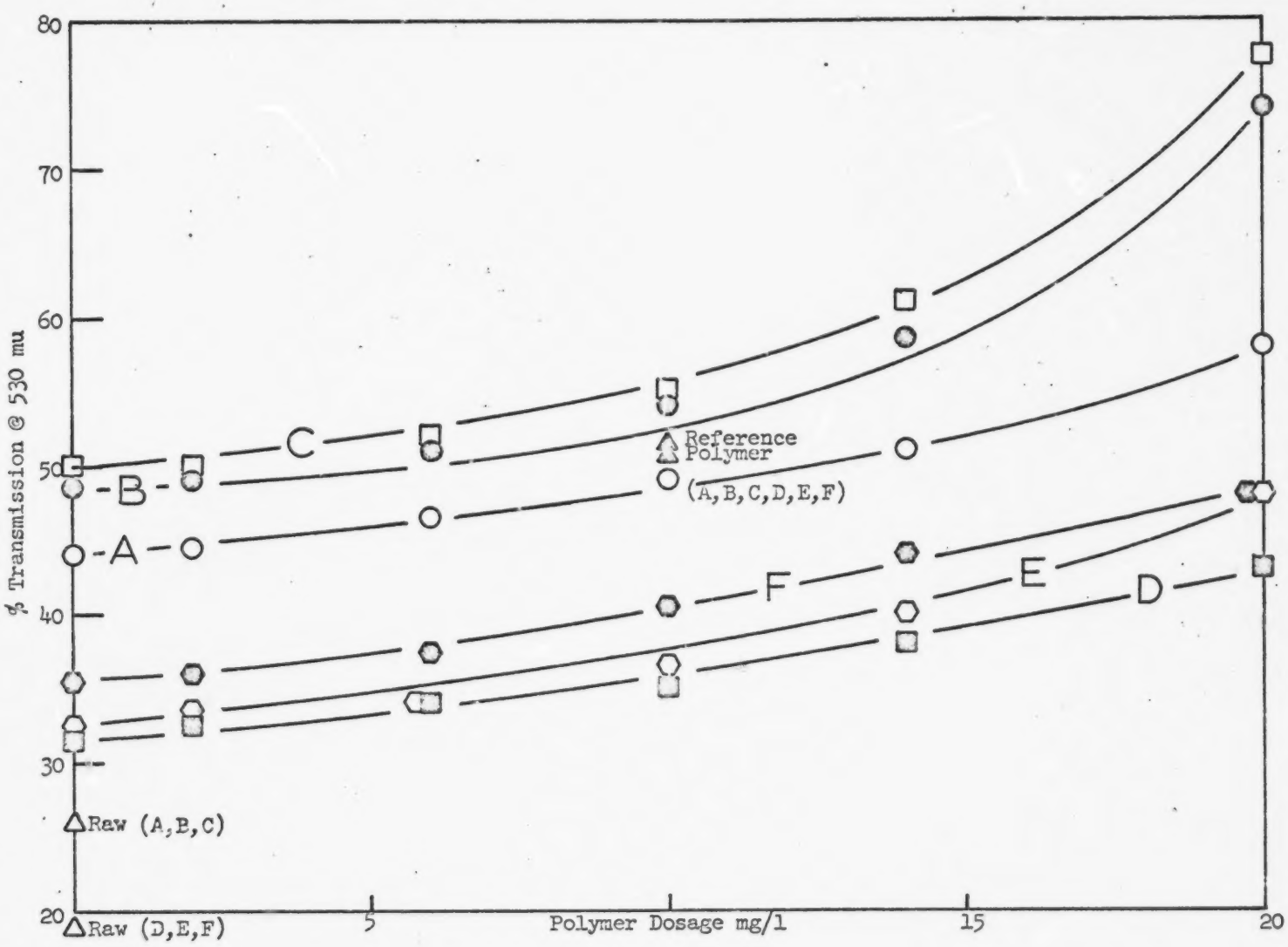

FIGURE 18. JAR TEST - POLYMERS #003-20A,B,C,D,E,F

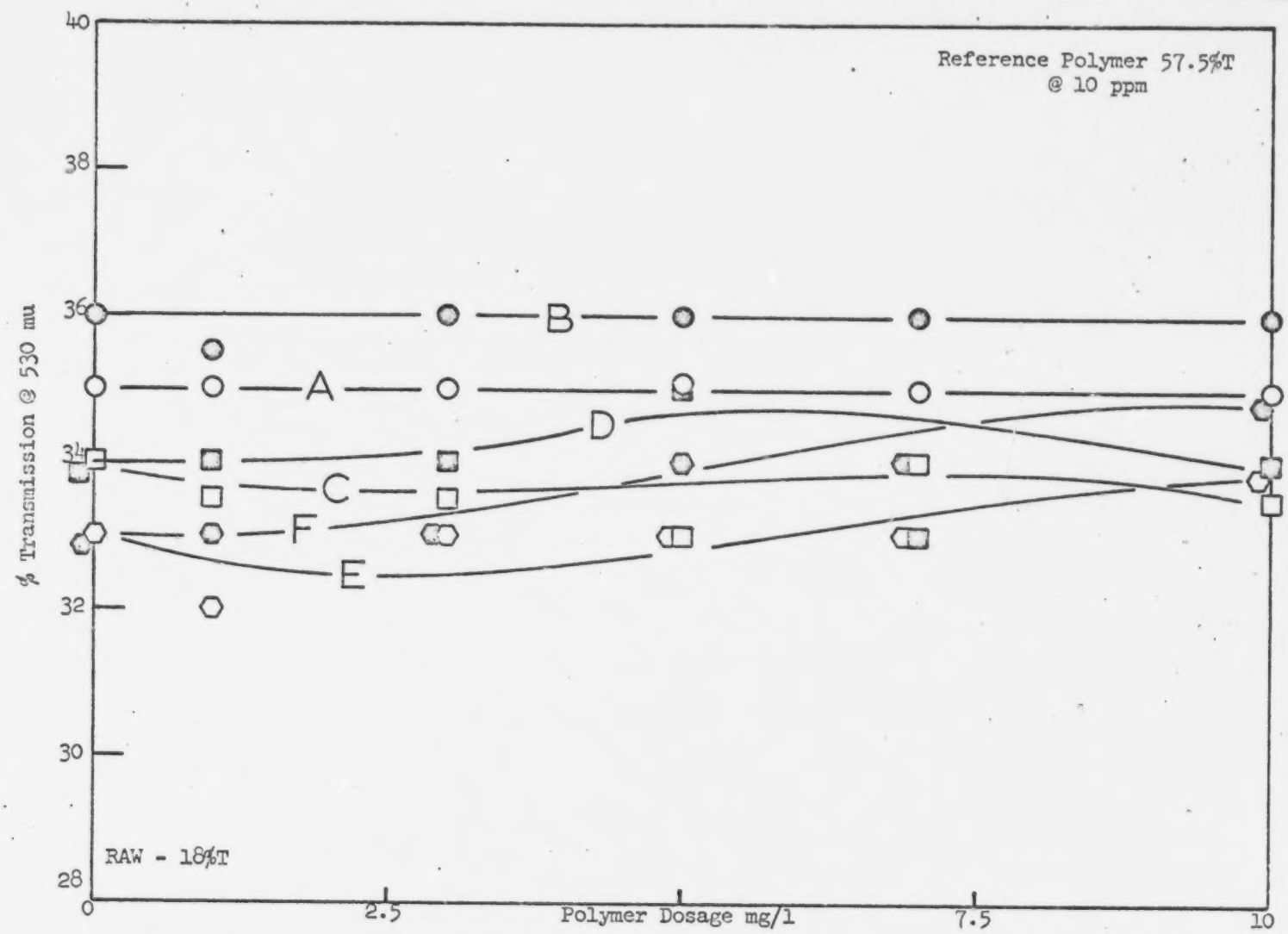

FIGURE 19. JAR TEST - POLYMERS #003-51A,B,C,D,E,F

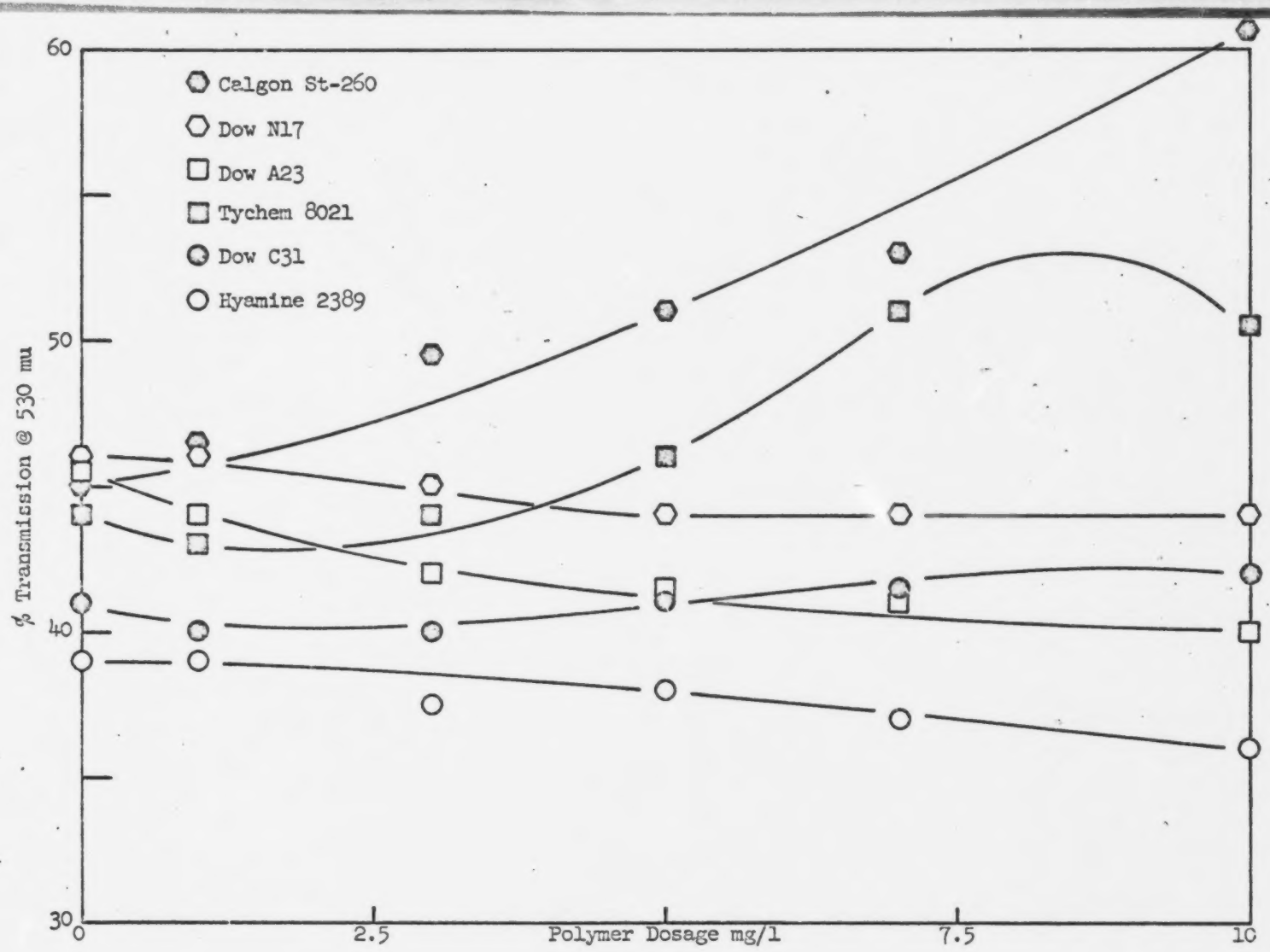

FIGURE 20. JAR TEST

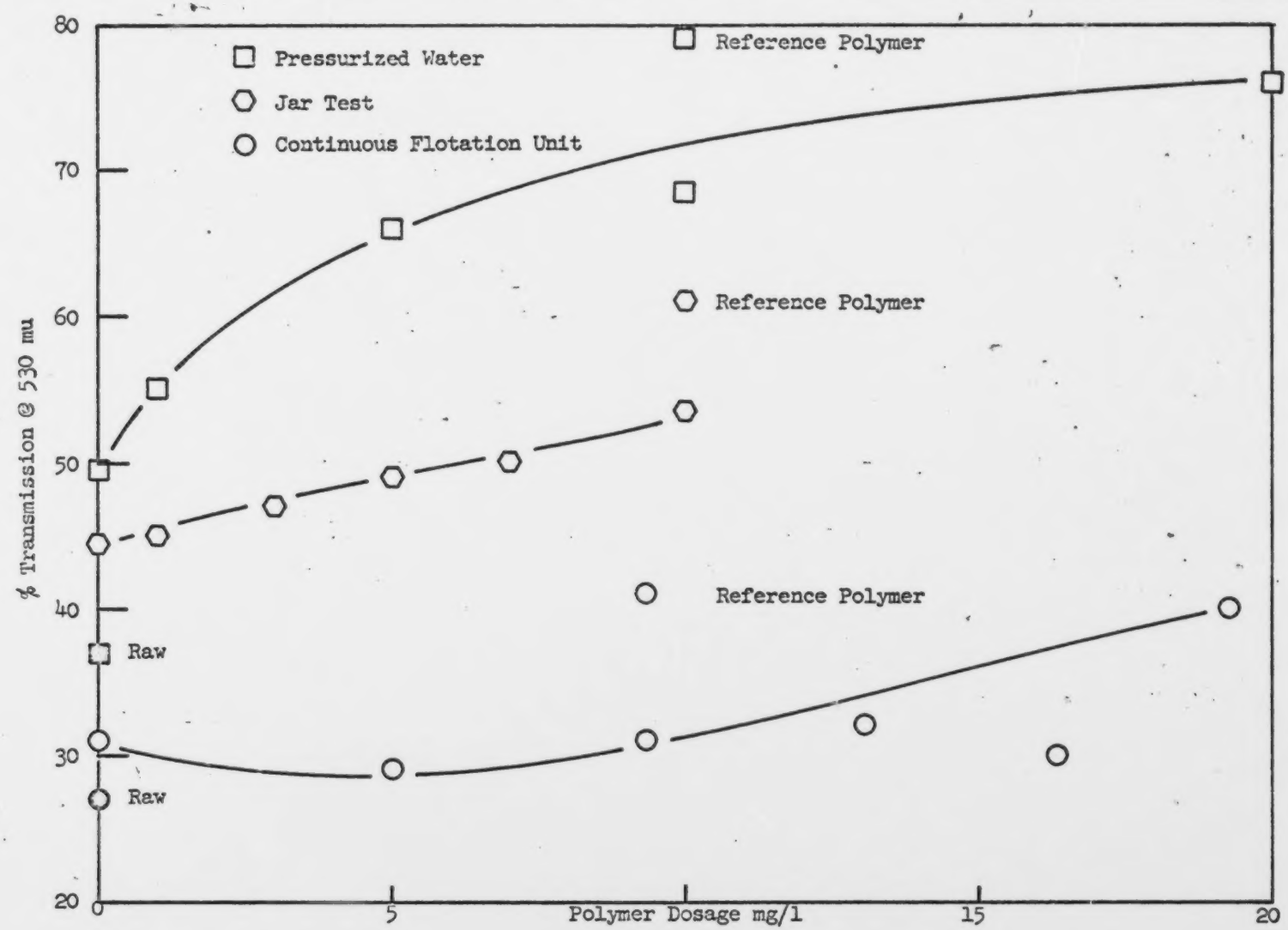

FIGURE 21. EVALUATION METHOD COMPARISON - PCLYMER #003-51D

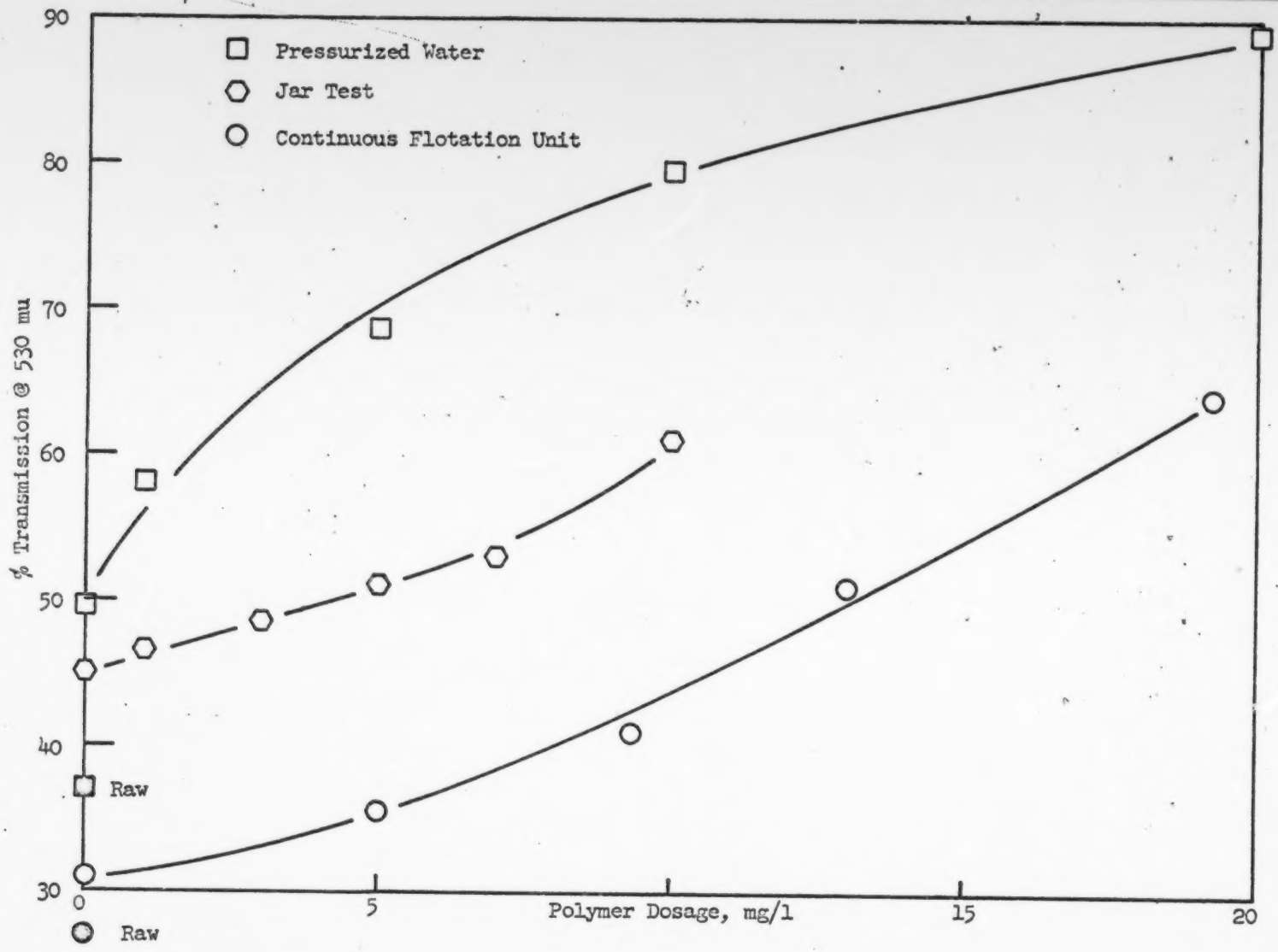

FIGURE 22. EVALUATION METHOD COMPARISON - REFERENCE POLYMER